ROBERTO JANNY TEIXEIRA JUNIOR

**ON GOVERNING EQUATIONS AND CLOSURE RELATIONS FOR THE MULTISCALE
MODELING OF CONCENTRATION POLARIZATION IN SOLID-OXIDE FUEL CELLS:
MASS TRANSFER AND CONCENTRATION-INDUCED VOLTAGE LOSSES**

São Paulo
(2017)

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Universidade de São Paulo para obtenção do título
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Orientador: Prof. Dr. José Luis de Paiva

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ABSTRACT

The aim of this dissertation is to appraise and critically reflect on the physical pertinence of governing equations and closure relations often used for the modeling of gas-phase transport phenomena in high-temperature solid-oxide fuel cells (SOFCs). More precisely, this work conducts a critical literature review on the concentration-induced voltage losses (*i.e.*, concentration polarization) resulting from mass transfer limitations. Thus, the overall object of this work was to stress awareness of the limits of mathematical models studied and developed in the SOFC literature to date, and which are specifically related to concentration polarization processes. To a great extent, the design of SOFC porous layers is likened to that of optimizing the transport of multicomponent gas mixtures in structured porous catalysts, for which diffusional and flow limitations are of cardinal importance. In both cases, severe inconsistencies in mass transport models cannot be simply ignored and the main uncertainties in utilizing such models should be clarified. It is hoped that the information herein will serve usefully to support future developments of more consistent theoretical frameworks, thereby improving the confidence on the results of numerical simulations.

The critical literature review has been carried out so to identify a number of physical inconsistencies, ill-defined approximations, and misleading mathematical derivations. Along the review, it is argued that the choice (or, more properly, the lack of conceptual refinement) of a particular mathematical model can significantly impair the “prediction” of transport processes relevant to concentration-induced power losses in SOFCs. One of the keystones of this work was therefore to re-interpret and thus to reassess the frequently contradictory literature related to certain classes of gas-phase transport models pertinent to the evaluation of concentration polarization. With this revisionary approach, it is expected that one could reduce confusion, clear up apparent contradictions, and improve the possibility of gaining new insights.

Keywords: Solid-oxide fuel cell. SOFC. Polarization. Mathematical modeling. Mass transfer. Diffusion. Porous media. Heterogeneous catalysis. Electrochemistry.

RESUMO

Esta dissertação tem o objetivo de avaliar e refletir criticamente sobre a pertinência física de equações de conservação e de relações de fechamento, frequentemente utilizadas na modelagem multiescala de fenômenos de transporte em células a combustível de óxido-sólido (SOFC). Dêu-se atenção especial ao escoamento em “microescala” de misturas gasosas multicomponentes, dentro de meios porosos quimicamente reativos. Em outras palavras, esta monografia busca ressaltar quais os limites para aplicação de certas classes de modelos matemáticos, os quais têm sido desenvolvidos e utilizados na literatura de SOFCs até o presente momento. O projeto de camadas porosas de SOFCs assemelha-se à tarefa de otimizar processos de transporte em catalisadores estruturados, para os quais a existência de limitações de transporte por difusão e por escoamento tem importância primordial. Por esta razão, inconsistências originadas em modelos de fenômenos de transporte não podem ser, simplesmente, negligenciadas e, portanto, as principais incertezas ao se utilizar tais modelos devem ser devidamente esclarecidas. Espera-se, com efeito, que as informações contidas neste trabalho sejam úteis para futuros desenvolvimentos teóricos mais consistentes, de forma a aumentar a confiabilidade no uso de resultados obtidos por simulações numéricas.

Palavras-chave: Célula a combustível de óxido-sólido. SOFC. Polarização. Modelagem matemática. Transferência de massa. Difusão. Meios porosos. Catálise Heterogênea. Eletroquímica.

ABBREVIATIONS

8YSZ	8 mol-% Y_2O_3 fully stabilized ZrO_2	RPD	Reaction Penetration Depth
ANN	Artificial Neural Network	RVE	Representative Volume Element
ASR	Area-Specific Resistance	SFR	Stagnation Flow Reactor
BOP	Balance of Plant	SOEC	Solid-Oxide Electrolysis Cell
BVE	Butler–Volmer Equation	SOFC	Solid-Oxide Fuel Cell
CFD	Computational Fluid Dynamics	TIP	Thermodynamics of Irreversible Processes
CHP	Combined Heat and Power	TPB	Three-Phase Boundary
CPIM	Cylindrical Pore Interpolation Model	WGS	Water-Gas Shift
DAE	Differential-Algebraic Equation	XCT	X-ray Computed Tomography
DGM	Dusty-Gas Model	YSZ	Yttria-Stabilized Zirconia (Y_2O_3 Stabilized ZrO_2)
EMF	Electromotive Force		
EPDM	Effective Porous Diffusion Model		
FEM	Finite Element Method		
FIB-SEM	Focus Ion Beam Scanning Electron Microscopy		
FVM	Finite Volume Method		
<i>GDC</i>	Gadolinium-doped Ceria		
LBGK	Bhatnagar-Gross-Krook model		
LBE	Lattice-Boltzmann Equation		
LBM	Lattice-Boltzmann Method		
LHS	Left Hand Side		
<i>LSCF</i>	Lanthanum Strontium Cobalt Ferrite		
<i>LSM</i>	Lanthanum Strontium Manganite		
MEA	Membrane-Electrode Assembly		
MFM	Modified Fick Model		
MIEC	Mixed Ionic–Electronic Conductor		
MSM	Maxwell-Stefan Model		
MTPM	Mean Transport Pore Model		
OCV	Open Circuit Voltage		
ODE	Ordinary Differential Equation		
PEM	Proton Exchange Membrane		
PEN	Positive-electrode/Electrolyte/Negative-electrode		
PFR	Plug Flow Reactor		
PPM	Parallel Pore Model		
RFR	Radial Flow Reactor		
RHS	Right Hand Side		

NOMENCLATURE

Lower-case Roman

Symbol	Meaning	Common Units
a_k	Chemical activity of the k -th species	Dimensionless
a_s	Specific-area density of active catalyst	cm^2/cm^3 , m^2/m^3
b_{core}	Thickness of grain boundary core (in an electric double-layer)	$\text{\AA}$
b_{ts}	Tafel slope	V
$\widetilde{\Delta c_p}$	Temperature-averaged change in heat capacity between products and reactants of a chemical reaction	$\text{J g}^{-1} \text{K}^{-1}$
$\bar{d}_p$	Average pore diameter	μm
e	Elementary charge ($\approx 1.6022 \times 10^{-19}$)	C
f_{an}	Effective anode microstructural multiplier	Dimensionless
f_{ca}	Effective cathode microstructural multiplier	Dimensionless
f_i	Distribution function of “fictitious” particles of gas, electron, or ion in the i -th (link) direction of momentum	kg m^{-3}
f_i^{eq}	Maxwellian local equilibrium distribution (population of particles in the direction of the i -th link)	kg m^{-3}
g	Gravitational acceleration	m s^{-2}
$h_{mres,k}$	Mass transfer coefficient of the k -th species	m s^{-1}
i	Overall current density	A cm^{-2}
i_F	Faradaic current density	A cm^{-2}
i_{dl}	Discharging current density of an electric double-layer	A cm^{-2}
i_T	Total current	A
i_F^V	Volume-specific faradaic current density (<i>i.e.</i> , transfer current)	A cm^{-3}
i_{dl}^V	Volume-specific double-layer current density	A cm^{-3}
$i_{\partial V}$	Total current per unit area normal to the z direction	A cm^{-2}
$i_F^{\partial V}$	Faradaic current flowing per unit area of the boundary of a three-dimensional electrode in the z direction	A cm^{-2}
$i_{dl}^{\partial V}$	Double-layer current flowing per unit area of the boundary of a three-dimensional electrode in the z direction	A cm^{-2}
i_*	Exchange current density evaluated/defined at reference conditions (<i>e.g.</i> , at the concentration C_{ref})	A cm^{-2}
i_*^V	Volumetric Exchange current density evaluated/defined at reference conditions (<i>e.g.</i> , at the concentration C_{ref})	A cm^{-3}
i_0	Exchange current density evaluated/defined at local gas composition	A cm^{-2}
i_0^V	Volumetric exchange current density evaluated/defined at local gas composition	A cm^{-3}
i_0^{TPB}	Exchange current density per unit of TPB length	A cm^{-3}
i_L (or i_{as})	Limiting (saturation) current density	A cm^{-2}
k	Chemical reaction rate constant (temperature-dependent)	s^{-1}

Symbol	Meaning	Common Units
k_0	Chemical reaction rate constant (temperature-independent)	s^{-1}
l_t	Active layer thickness	μm
l_{elyt}	Electrolyte thickness	μm
l_N	Newman's reaction penetration depth	μm
$\hat{l}_\delta$	Dimensionless current density	Dimensionless
$\hat{l}_v$	Dimensionless exchange current density	Dimensionless
$\hat{l}_q$	Dimensionless parameter that indicates the effect of mass transport of reacting molecular species	Dimensionless
$\tilde{m}_T$	Total molar flow rate of fuel and diluent	$mol\ s^{-1}$
n_{ad}	Number of available surface sites for gas adsorption	$sites\ cm^{-2}$
n_k	Particle number density of the k -th species	$particles\ m^{-2}$
$\vec{n}$	Outward pointing unit vector to a given interface	Dimensionless
p	Total thermodynamic pressure (also taken as being equal to the mechanical pressure, if not stated otherwise)	Pa, bar
p_k	Partial pressure of the k -th gas species	Pa, bar
p_x	Partial pressure of the diffusion-limited species	Pa, bar
$\dot{q}_i$	Superficial source term (net reaction rate) of the i -th reaction	$kmol\ m^{-2}\ s^{-1}$
$\langle r_p \rangle$	Mean transport pore radius	μm
$\bar{r}_p$	Average pore size	μm
u	Gas flow axial velocity	$m\ s^{-1}$
$\bar{u}_T$	Mean thermal velocity of the gas	$m\ s^{-1}$
u_s	Superficial velocity in porous medium domain	$m\ s^{-1}$
u_{mix}	Mixture velocity in the gas channel (fuel or air channels)	$m\ s^{-1}$
x_k	Mass fraction of the k -th species	Dimensionless
y_k	Mole fraction of the k -th species	Dimensionless
z_e	Number (in moles) of electrons exchanged per mole of fuel (or oxidant)	Dimensionless

Upper-case Roman

Symbol	Meaning	Common Units
$\mathcal{A}_c$	Cross-section area	m^2
A_C	Transport resistivity in CPIM (defined by Eq. 4.50b)	$s\ m^{-2}$
A_K	Transport resistivity in CPIM (defined by Eq. 4.50c)	$s\ m^{-2}$
ASR	Area-specific resistance of the cell	$\Omega\ m^2$
B	Permeability coefficient (different models)	m^2
B_o	Permeability coefficient (EPDM model)	m^2
B''_{MTPM}	Darcy Law's permeability coefficient (MTPM model)	$m^2\ s^{-1}$
$\mathcal{C}_{dl}$	Double-layer capacitance	$\mu F\ cm^{-2}$

Symbol	Meaning	Common Units
C_{fo}	Forchheimer coefficient	m^{-1}
C_k	Molar concentration of the k -th gas species	$mol\ m^{-3}$
C_{fg}	Feed gas molar concentration	$mol\ m^{-3}$
C_g	Total molar concentration (molar density)	$mol\ m^{-3}$
C_{ref}	Gas molar concentration at reference conditions	$mol\ m^{-3}$
$D_{i,j}$	Binary (<i>i.e.</i> , mutual) diffusivity	$m^2\ s^{-1}$
$D_{k,i}^A$	MS diffusivity in CPIM (defined by Eq. 4.50f)	$m^2\ s^{-1}$
$\mathcal{D}_k^{eff}$	Effective diffusion coefficient of the k -th species	$m^2\ s^{-1}$
D_{km}	Mixture-average diffusion coefficient for the k -th species in the gas mixture	$m^2\ s^{-1}$
D_k^{surf}	Surface diffusion coefficient of the k -th species	$m^2\ s^{-1}$
D_s	Surface diffusion coefficient in the limit of low coverage	$m^2\ s^{-1}$
E	“Generic” electromotive force (EMF) (see Eq. 2.67 and 2.68)	V
E_{cell}	Fuel cell operating voltage	V
E_{rev}	Fuel cell reversible (“thermodynamic”) voltage	V
E_{OCV}	Open circuit voltage	V
E_{loss}	Overall value of voltage losses	V
E_H	As defined in Eq. (2.10)	V
E^∇	Fuel cell voltage at a specified standard (reference ∇) state	V
E_0	Activation energy	$J\ mol^{-1}$
$\mathcal{F}$	Faraday constant (≈ 96485)	$C\ mol^{-1}$
F_D	Drag force source term in porous medium	$N\ m^{-3}$
$\overrightarrow{\Delta G}^\ddagger$	Actual chemical barrier associated with forward reaction when modulated by the presence of an electrical field	$J\ mol^{-1}$
$\overleftarrow{\Delta G}^\ddagger$	Actual chemical barrier associated with reverse reaction when modulated by the presence of an electrical field	$J\ mol^{-1}$
$\widetilde{\Delta_r G}$	Overall (specific) change in Gibbs energy of reaction that is modulated by the presence of an electrical field	$J\ mol^{-1}$
$\Delta_r G$	Total (specific) change in Gibbs energy of reaction	$J\ mol^{-1}$
$\Delta_r G^\nabla$	Total (specific) change in Gibbs energy of reaction at a specified standard (reference ∇) state	$J\ mol^{-1}$
$\Delta_f G$	Total (specific) Gibbs energy of formation	$J\ mol^{-1}$
$G_{f k}$	Specific Gibbs energy of formation of the k -th species	$J\ mol^{-1}$
$\mathcal{H}_{ch}$	Height of flow channel	m
$\Delta_r H$	Total (specific) change in the enthalpy of the electrochemical reaction	$J\ mol^{-1}$
$\tilde{J}_k$	Diffusive molar flux of the k -th species relative to the mass-average velocity	$mol\ m^{-2}\ s^{-1}$
J_k	Diffusive mass flux of the k -th species relative to the mass-average velocity	$kg\ m^{-2}\ s^{-1}$
$K_{O_i^{2-}}$ and $K_{O_s^{2-}}$	Mass action (quasi-equilibrium) constants	$bar^{1/2}$
L	Characteristic length scale of the problem	m
L_{ch}	Length of the flow channel	m

Symbol	Meaning	Common Units
L_s	Characteristic length of electrode's microstructure surface, representing a "diffusion length" (microstructural parameter)	m
M_k	Molar mass of the k -th species	g gmol ⁻¹
$\bar{M}_n$	Number-average molar mass	g gmol ⁻¹
$\bar{M}_w$	Mass-average molar mass	g gmol ⁻¹
$M_{\Delta n,k}$	Relative molar mass of the k -th species with respect to the number-average molar mass	Dimensionless
$\mathcal{N}_a$	Avogadro constant ($\approx 6.022 \times 10^{23}$)	mol ⁻¹
$\mathcal{N}_{gas}$	Total number gaseous species	Dimensionless
$\mathcal{N}_{reac}$	Total number of chemical/electrochemical reactions	Dimensionless
$\mathcal{N}_{spe}$	Total number chemical species (gaseous, surface, or solid bulk species)	Dimensionless
$\tilde{N}_k$	Total molar flux of the k -th species	kmol m ⁻² s ⁻¹
N_k	Total mass flux of the k -th species	kg m ⁻² s ⁻¹
$\mathcal{P}_e$	Channel perimeter	m
$\mathcal{R}$	Ideal gas constant (≈ 8.314)	J K ⁻¹ mol ⁻¹
R_{OR}	Electrochemical (oxidation) reaction rate	gmol cm ⁻³ s ⁻¹
$\dot{S}_{S,\rho k}$	Superficial source term in the species conservation equation (written in terms of mass densities)	kg m ⁻² s ⁻¹
$\dot{S}_{S,C_k}$	Superficial source term in the species conservation equation (written in terms of molar densities)	kmol m ⁻² s ⁻¹
$\dot{S}_{V,m}$	Volumetric source term in continuity equation	kg m ⁻³ s ⁻¹
$\dot{S}_{V,v}$	Volumetric source term in momentum equation	N m ⁻³ s ⁻¹
$\dot{S}_{V,x_k}$	Volumetric source term in the species conservation equation (written in terms of mass fractions)	kg m ⁻³ s ⁻¹
$\dot{S}_{V,y_k}$	Volumetric source term in the species conservation equation (written in terms of mole fractions)	kmol m ⁻³ s ⁻¹
$\dot{S}_{V,\rho k}$	Volumetric source term in the species conservation equation (written in terms of mass densities)	kg m ⁻³ s ⁻¹
$\dot{S}_{V,C_k}$	Volumetric source term in the species conservation equation (written in terms of molar densities)	kmol m ⁻³ s ⁻¹
$\dot{S}_{V,\tilde{\mu}}$	Volumetric source term in Nernst-Einstein equation	A m ⁻³
$\dot{S}_{V,\phi}$ (or $\dot{S}_{V,i}$)	Volumetric source term in the charge conservation equation	A m ⁻³
$\Delta_r S$	Total (specific) change in entropy of reaction	J K ⁻¹ mol ⁻¹
$\Delta_r S^\ominus$	Total (specific) change in entropy of reaction at a specified standard (reference $\ominus$) state	J K ⁻¹ mol ⁻¹
T	Absolute temperature	K
$\mathcal{U}_{fu}$	Fuel utilization factor	Dimensionless
V	Mass-average velocity	m s ⁻¹
V_k	Velocity of the k -th species	m s ⁻¹
Y	Characteristic length defined in Eq. 3.46	m
Y_*	Dimensionless characteristic length defined in Eq. 3.52	Dimensionless

Lower-case Greek

Symbol	Meaning	Common Units
α_a (or $\tilde{\alpha}$)	Anodic transfer coefficient (symmetry factor) in the BVE	Dimensionless
α_c (or $\tilde{\alpha}$)	Cathodic transfer coefficient (symmetry factor) in the BVE	Dimensionless
δ_{kl}	Kronecker delta	Dimensionless
δ_{an}	Thickness of porous anode	μm
δ_{ca}	Thickness of porous cathode	μm
δ_{diff}	Diffusion layer thickness	μm
δ_{DL}	Thickness of space charge region (symmetric double layer)	$\text{\AA}$
δ_{GB}	Thickness of grain boundary	$\text{\AA}$
δ_s	characteristic length confining the active region for adsorption/diffusion processes	μm
ε	Effective porosity ("open porosity" or percolated porosity)	Dimensionless
ϵ	Dimensionless Newman's reaction penetration depth (RPD)	Dimensionless
ϵ_{cell}	Actual efficiency (ϵ_{cell}) of the fuel cell	Dimensionless
ϵ_{max}	Maximum efficiency ("thermodynamic efficiency")	Dimensionless
η	Augmented polarization	V, mV
η_0	Voltage required to completely convert i , from ionic into electronic form, within the active layer of an electrode	V, mV
η_{act}	Activation polarization	V, mV
$\eta_{A,an}$	Anodic contribution of activation polarization	V, mV
$\eta_{A,ca}$	Cathodic contribution of activation polarization	V, mV
η_{conc}	Concentration polarization	V, mV
$\eta_{C,an}$	Anodic contribution of concentration polarization	V, mV
$\eta_{C,ca}$	Cathodic contribution of concentration polarization	V, mV
$\eta_{C,BV}$	"Kinetic" loss (concentration-induced kinetic losses)	V, mV
$\eta_{C,Nernst}$	Nernstian loss	V, mV
η_{leak}	Electronic Leakage	V, mV
η_{ohm}	Ohmic polarization	V, mV
λ_{stch}	Fuel stoichiometry in the electrochemical reaction	Dimensionless
λ_{tpb}	TPB length per unit volume of porous electrode (TPB density)	$\mu\text{m}/\mu\text{m}^3$
μ_k	Chemical potential of the k -th species	J mol^{-1}
$\tilde{\mu}_k$	Electrochemical potential of the k -th species	J mol^{-1}
μ_m	Mixture-averaged dynamic viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
ν_g (or ν_m)	Mixture-averaged kinematic viscosity	$\text{m}^2 \text{s}^{-1}$
σ	Electrical conductivity	S m^{-1} , S cm^{-1}
σ_k^{surf}	"Equivalent" surface mole fraction of the k -th species	Dimensionless
τ	Tortuosity	Dimensionless
τ_*	Tortuosity factor	Dimensionless
τ_c	Relaxation time towards local equilibrium	Dimensionless

Symbol	Meaning	Common Units
ν_k	Net stoichiometric coefficient of the k -th species	Dimensionless
ν'_k	Stoichiometric coefficient for the k -th species being a reactant	Dimensionless
ν''_k	Stoichiometric coefficient for the k -th species being a product	Dimensionless
$\nu_{k,i}$	Net stoichiometric coefficient of the k -th species participating in the i -th reaction	Dimensionless
ρ_{elyt}	Electrical (ohmic) resistivity of electrolyte layer	$\Omega \text{ m}$
ρ_g	Mixture-average mass density of the gas mixture	kg m^{-3}
ρ_k	Mass density of the k -th species in the gas mixture	kg m^{-3}
ϕ	Electrostatic potential	V
$\Delta\phi$	Actual (imposed) electrode potential step	V
$\Delta\phi_{eq}$	Equilibrium electrode potential step (Galvani potential)	V
$\Delta\phi_s$	Potential difference between the electronic conductor and the adsorbed layer	V
$(\Delta\phi_s)_{max}$	Surface potential step when O_{ad}^{2-} reaches full site occupancy	V
ψ	Electric potential due to charge separation	V
Ψ_{str}	Structural factor in the MTPM	Dimensionless
χ	Electric potential due to dipole orientation	V
ϖ_{km}	Reduced molar mass of the k -th species	Dimensionless

Upper-case Greek

Symbol	Meaning	Common Units
$\mathfrak{B}$	Darcy Law's permeability	$\text{kg m}^{-3} \text{ s}^{-1}$
Γ	Available surface site density	mol cm^{-2}
$\Gamma_{elde(tpb)}$	Density of "active" surface sites near the TPB region	mol cm^{-2}
Θ	Dimensionless surface site (coverage) fraction occupied by ad-ions or ad-atoms	Dimensionless
$\mathfrak{X}_k$	chemical symbol for the k -th species (<i>e.g.</i> , fuel, oxidizer, inert)	-
$\mathfrak{m}$	Reference/standard state	-

Superscripts

Symbol	Meaning
<i>bulk</i>	Denotes a value evaluated at bulk gas conditions
<i>eff</i>	Effective property
<i>Kn</i>	Knudsen
<i>MS</i>	Maxwell-Stefan model
<i>DGM</i>	Dusty Gas model
<i>tpb</i>	Denotes a value evaluated at the three-phase boundary
*	Reference quantity

Subscripts

Symbol	Meaning
<i>ad</i>	Adsorbed species (<i>i.e.</i> , concerning an adsorbed monolayer)
<i>an</i>	Anode
<i>ca</i>	Cathode
<i>dl</i>	Electric double-layer
<i>e</i>	Electronic phase/conductor
<i>elde</i>	Electrode (anode or cathode)
<i>elyt</i>	Electrolyte
<i>eq</i>	Equilibrium
<i>io</i>	Ionic phase/conductor
<i>rev</i>	Reversible
<i>an/elyt</i> (or <i>ae</i>)	Anode/electrolyte interface (may also represent an anodic TPB hot spot)
<i>ca/elyt</i> (or <i>ce</i>)	Cathode/electrolyte interface (may also represent a cathodic TPB hot spot)

Dimensionless Groups

Symbol	Meaning
<i>Kn</i>	Knudsen number
<i>Pe</i>	Peclet Number
<i>Pr</i>	Prandtl Number
<i>Re</i>	Reynolds number
<i>Sh</i>	Sherwood number
<i>Sc</i>	Schmidt number

Other Nomenclature

- Symbols with circumflex or hat accent (*i.e.*, $\hat{}$) marks a dimensionless quantity
- Symbols with overbar (*i.e.*, $\overline{}$) marks an averaged quantity

CONTENTS

ABSTRACT	IV.
RESUMO	V.
ABBREVIATIONS.....	VI.
NOMENCLATURE	VII.
CHAPTER 1: GENERAL INTRODUCTION AND BACKGROUND	1.
1.1 Aim of this Dissertation Work.....	1.
1.2 Chapter Organization	5.
1.3 Solid-Oxide Fuel Cells (SOFCs)	6.
1.3.1 Overview of SOFCs	6.
1.3.2 SOFC Components and Functionality	9.
1.3.3 SOFC Designs	12.
1.3.4 Brief Introduction to SOFC Materials and Fuel Processing	15.
1.4 Mathematical Modeling of Solid-Oxide Fuel Cells	21.
1.4.1 Modeling on the Single-Cell Scale	22.
1.4.2 Concepts on Multiscale Modeling and Multiphysics Simulation	26.
1.4.3 Mass Transfer in Chemically Reacting Gas Flows	30.
1.4.4 Electrochemical System.....	34.
CHAPTER 2: ON THE PHYSICAL CHEMISTRY OF SOFCS.....	35.
2.1 Fuel Cell Equilibrium Thermodynamics	35.
2.1.1 The Open Circuit Voltage (OCV)	36.
2.1.2 Fuel Cell Efficiency.....	37.
2.1.3 Nernst Equation	38.
2.2 Fuel Cell Irreversibilities (Losses or Polarizations)	40.
2.2.1 Causes of Voltage Drop	42.
2.2.2 Distinguishing and Combining Different Irreversibilities	45.
2.3 Theoretical Considerations and Inconsistencies in Defining SOFC Polarizations	51.
2.3.1 Clarifications on Polarizations and Potential Steps	51.
2.3.2 Macroscopic Calculation of Activation Polarization	59.
2.3.3 Active Layer, Penetration Depth, and Perfect-Electronic-Conductors	66.
2.3.4 Disambiguation of Activation, Concentration, and Augmented Polarizations	74.

CHAPTER 3: MASS TRANSFER LIMITATIONS AND CONCENTRATION LOSSES	82.
3.1 Introduction	82.
3.2 Preliminaries on Concentration Polarization	84.
3.3 Thermostatistics of Concentration Polarization	86.
3.3.1 Concentration Cell and “Virtual Balance” of Electrochemical Potentials	86.
3.3.2 Possible Effects of Surface Ad-ions on Concentration Polarization	90.
3.4 Concentration-induced Nernstian Losses	100.
3.4.1 Losses along Electrode’s Through-Plane Direction.....	100.
3.4.2 Losses along Mean Flow Direction (Reactant Depletion in Gas Channels).....	103.
3.5 Concentration-induced Kinetic Losses	105.
3.6 Brief Digressions on Mass Transport and Cross-Effects.....	108.
CHAPTER 4: MODELING TECHNIQUES IN CONCENTRATION POLARIZATION	116.
4.1 Introduction	116.
4.2 System-Level Models: Uniivariate and Multivariate Modeling	118.
4.3 Single-Scale Models I: Qualitative Analytical Modeling	123.
4.3.1 Kulikovsky’s Model for the Active Layer	124.
4.3.2 Kulikovsky’s Quasi-2D Model of a Single-Cell.....	128.
4.4 Single-Scale Models II: Semi-Empirical Analytical Modeling	129.
4.4.1 Parametric Models and Extraction of Physical Parameters	129.
4.4.2 Effective Porous Diffusion Models (EPDMs)	130.
4.5 Single-Scale Models III: Multiphysics Macro-Homogeneous Approach	140.
4.5.1 Macro-Homogeneity of Field Equations in an Inhomogeneous Continuum	142.
4.5.2 Macro-Homogeneous Models of Porous SOFC Layers	144.
4.5.3 Some Concluding Remarks on Macro-Homogeneous Models	170.
4.6 Single-Scale Models IV: Multiphysics in Mesoscale (and Beyond)	172.
4.6.1 Geometrical Modeling and Reconstruction of Porous Electrodes	173.
4.6.2 Structure-Resolved Models of Gas Transport in Porous SOFC Layers	177.
4.7 Multiscale Models I: Macroscale Models Informed by Microscale Correlations	188.
4.8 Multiscale Models II: Macroscale Models Informed by Microscale Simulations	188.
4.9 Multiscale Modeling Principles, Multiscale Homogenization, and Hybrid Methods.....	190.
4.10 Reactor (Gas Channel) Models	193.
4.10.1 Button-Cell Reactor and Impinging Wall Jet Flows	193.
4.10.2 Simplified Models (PFR, SFR, RFR)	196.
CHAPTER 5: CONCLUSIONS AND OUTLOOK.....	204.
APPENDIX A — PROOFS AND DERIVATIONS.....	208.
BIBLIOGRAPHY	231.

Chapter 1

GENERAL INTRODUCTION AND BACKGROUND

1.1 Aim of the Dissertation Work

The analysis of solid-oxide fuel cell (SOFC) operation is a technically challenging task, which involves the appraisal of multiple chemical and physical phenomena that cannot be assessed under a single scientific paradigm, thus requiring multi-physics tools for the credible description of SOFC behavior. In this regard, mathematical modeling and numerical simulation constitute a valuable tool in the evaluation of multi-physics phenomena in SOFCs, inasmuch as one can examine, in a relatively straightforward manner, the effects of different design parameters and operating conditions on fuel cell performance. Furthermore, in situations where multiple physical scales play a part, this performance is also governed by the interplay of microscopic processes whose simultaneous interaction can give rise to complex (and often nonintuitive) coupling effects associated to disparate space and time scales, ultimately affecting the macroscopic (“experimentally observable”) performance of SOFCs. It is thus unlikely that simplified single-scale models are able to accurately depict the performance of all individual components of a system (see Fig. 1.1), when the macroscale manifestation of microscale physics stem from such complex process convolution. In this case, the competence to make an otherwise scale-resolved appraisal of SOFC operation relies on a multiscale modeling approach^[1, 2].

Although truly faithful multiscale models of any complete fuel cell system are in principle impossible to attain, excess use of empiricisms and usage of distributed-parameter models in the SOFC literature (*i.e.*, when these are misused and misinterpreted) help to further obscure the physical meaning of a number of natural processes that one is trying to describe, thus precluding a reliable interpretation of both numerical simulation results and experimental data. In this context, it is expected that this dissertation work will provide a useful contribution and fulfill the particular need for a better theoretical judgment of a few but important topics related

to the computational modeling of gas-phase transport phenomena, which are necessary to the evaluation of concentration polarization (concentration-induced voltage losses) in high-temperature SOFCs. By bringing the discussion of such topics to the fore, one hopes to unveil the strong contrast between the real complexity of SOFCs and the crudity of some of the mathematical modeling techniques frequently used in the literature.

Figure 1.1: Scheme illustrating the multiscale nature of a SOFC (picture reproduced from [3]).

During the laborious task of understanding and reviewing the body of literature, it was found that many pertinent remarks and critical assessments on mass transport, relevant to SOFC modeling, had been already drawn by authors from late 50's until late 90's. However, equally many of those findings have been either obscured over the years or disregarded by unfavorable, cursory analyzes. Therefore, although limiting the literature review to only recent and high impact publications constitutes a prolific research path, a drawback of this choice is the possibility to stumble upon some "vicious circle" of a defective theory or model. In this case, presumably, "hidden issues" remain to be dealt with at a later time, as appear necessary to the researcher concerned enough to controvert the views on that theory. On the other hand, the in-depth scrutiny of all current theories on mass transport constitutes a near impossible undertaking. Such endeavor would certainly entail an overwhelming store of existing knowledge, and for this reason an all-embracing scrutiny of existing theories was not pursued in this dissertation. Moreover, it would be also a substantial undertaking to overturn the vested assumptions (and long-held preconceived interests) of an entire class of consolidated modeling frameworks that have been produced by scholars from past generations.

Therefore, neither new mass transfer theories will be introduced nor will be the existing theories significantly advanced in the pages that follow. This is to say that the present work is not about the much-needed critical review and reconciliation of the phenomenological theory of transport phenomena with the results from statistical mechanics or extended non-equilibrium thermodynamic theories. Even though the current distance between applied mathematicians/physicists and engineers (especially chemical engineers) has become somewhat large, with the current macroscale phenomenological theory still mired in misleading and erroneous assumptions made by previous models devised at the beginning of 20th century¹, the analyses in this work have been confined to a chiefly revisionary character, covering only an superset of existing modeling techniques that have been applied specifically in the SOFC literature, without scrutinizing, however, the actual theoretical foundation on which such techniques has been built.

The fact that more fundamental underlying theories (which, as mentioned above, are fallible to their nature) will not be analyzed in this work does not prevent the author from critically reviewing and appraising, without significant loss of pertinence and generality, the mathematical models that were developed using these theories in order to assess concentration polarization effects in SOFCs. The justifying reason is that these mathematical models have been, nevertheless, successfully applied to understand and predict natural processes of scientific and engineering interest in the field of SOFC research. That said, however, and more so given that the limitations of the founding theory are not well known, these modeling techniques are not without identifiable trade-offs and, first and foremost, without limits of validity. Thus, even though the scrutiny of existing mass transfer theories is not a plausible alternative in this dissertation, one should still justify the physical pertinence and perceive the uncertainties of derived mathematical models (“superset of modeling techniques”). With such critical perspective, it is of interest of this work to revisit a number of models on transport phenomena that have been applied to the modeling of mass transport in SOFCs, motivated by the following concerns and considerations:

- I. Try to identify ambiguities when evaluating “cause-effect” relations, which are typical of lumped (distributed) parameter models. On this wise one would be able to properly recognize what factors are causing the system to behave in one way and not another. This level of distinction is relevant from both equipment engineering and optimization perspectives. Even though there are times when a simplified description for the physical system is necessary, the undervaluation of model’s simplifying assumptions may render experimental conclusions biased.

¹ Some of the shortcomings of the so-called (linear) phenomenological transport theory, or of any theory based on the macroscale-continuum hypothesis, are related to the inability or limitation of this theory in accounting for the fact that the properties of gas systems can depend on the details about the magnitude and motions of their more basic constituents (molecules).

- II. Discuss mathematical models for their advantages and limitations (*i.e.*, trade-offs), taking into consideration the credibility of model predictions based on the evidence of uncertainties that are associated with modeling errors. Ultimately, this should permit a more accurate picture of fuel cell macroscale performance.
- III. It is plausible (and practical) that physical models may have a number of undisclosed assumptions and emphasis not spelled out in words that are, at some level, familiar to those researchers accustomed to the scientific field wherein these models have been applied. The disciplined use of simplifying assumptions (that is, to make a simplifying assumption based on substantiated grounds) necessarily involves, to some extent, a bit of common sense (within that particular scientific field) and also some “educated guess” about the importance (impact) of the specific assumption being made. However, if one fails to disclose a large number of important physicochemical assumptions, rationalized hypotheses are irretrievably shadowed by fallacious arguments. Thus, a simplifying assumption can only be that which allows simplifying the analysis and must not affect the physicochemical behavior one is trying to examine or demonstrate. In other words, it must not constitute a critical assumption that can undermine the proper description of that behavior.

Most of the developments in **Chapter 4** are in the lines of what was just introduced above, which is of a critical review driven by the importance of thoroughly understanding the model’s assumptions, including the identification of possible physical inconsistencies, ill-defined approximations, and misleading mathematical derivations, where these are deemed as relevant factors in the model prediction capability. On the other hand, the discussions presented in **Chapter 2** (more precisely in §§2.3) and in **Chapter 3** (more precisely in §§3.3) go beyond the mere revisionary task; instead they propose some new analyses whose appeal is chiefly theoretical and whose value is the disambiguation of important concepts often misprized and/or misrepresented in the SOFC literature, but which are nonetheless critical to the proper definition and thus the evaluation of concentration-induced voltage losses.

Finally, it should be (once more) underlined that this work lacks a focused assessment of multicomponent mass transfer theories based on idealized “capillary pore spaces”, which are frequently used as a modeling abstraction for the pore-level information in macroscale phenomenological models. In this respect, the description of what (supposedly) occurs at the pore level represents additional sources of flagrant oversimplifications (*i.e.*, misrepresentations of transport processes) made by many SOFC models, potentially undermining the correct evaluation of SOFC macroscale performance. This most critical topic is, however, beyond the scope of this dissertation. Even though the present work certainly establishes a relevant academic territory, it also readily recommends further research by acknowledging the previously mentioned limitation.

1.2 Chapter Organization

This work has been subdivided into four (4) main chapters and a final chapter in which overall conclusions are drawn and an outlook for future works is proposed. These main chapters may be summarized as follows:

- Chapter 1 (General Introduction): this chapter starts with a short introduction to solid-oxide fuel cell, its components, its principles of operation, and its key design features, all of which constitute a very basic and yet still necessary knowledge for understanding the physicochemical processes that will be addressed in later chapters. However, in order to not lose sight of the purpose of this work, these initial sections have been kept as simple as possible. Besides introducing more formal aspects of SOFCs, this chapter also provides an overview of what will be examined in the next chapters concerning the mathematical modeling of (single-cell) SOFCs.
- Chapter 2 (Preliminaries on the Physical Chemistry of SOFCs): the general (macroscopic) equilibrium thermodynamics of SOFCs is presented, followed by a short description of the main forms of irreversibilities (usually referred to as polarizations) associated with cells operating out of equilibrium. These polarizations ultimately lead to irreversible power losses, which are often quantified as voltage drops with respect to the cell reversible (“maximum”) thermodynamic voltage. A theoretical discussion has also been prepared on the precise definition of SOFC polarizations in order to pinpoint a number of inconsistencies found in the literature.
- Chapter 3 (Mass Transport Limitations and Concentration Losses): in this chapter the main topic of concentration-induced voltage losses (“concentration polarization”) is introduced, wherein the concept of mass (and possibly momentum) transport limitations is related to other SOFC properties and processes such as electrochemical potentials, limiting (or saturation) current densities, Nernstian losses, kinetic (or surface overvoltage) losses, and other “less common” types of mass transfer cross-effects (e.g., Soret-Dufour and mechano-chemical effects).
- Chapter 4 (Modeling Techniques for Concentration Polarization): this chapter discusses the modeling techniques commonly used in the SOFC literature that are concerned to the evaluation of concentration polarization. The discussion is centered on governing equations and closure relations pertinent only to the “gas-phase” (i.e., to reactive multicomponent gas flow). Inevitably, though, electrochemical reactions and charge transport are addressed as well for the sake of information completeness and contextualization of the problem being modeled (however, these topics are not treated at length since they are not the focus of this work). This section is in the lines of a “critical review”, serving the purpose of highlighting opportunities for improvement and clarification of existing models.

1.3 Solid-Oxide Fuel Cells (SOFCs)

1.3.1 Overview of SOFCs

Fuel cells have their origin in the conceptual idea of an efficient two-step fuel combustion process with generation of charged species as intermediates, as first asserted in 1839 by the Swiss scientist Christian Friedrich Schoenbein, and later on materially realized by Sir William Grove^[4], who in the same year published the experimental observation of voltage in a concentration cell (when combining hydrogen and oxygen gases in the presence of platinum). The realization that fuel cells could theoretically produce electricity in a more efficient way than conventional (*i.e.*, without bottoming-cycle) thermal engines was possible just after electrochemistry was connected with thermodynamics, in the end of the nineteenth century. Certainly, this finding became a captivating force drawing research and development efforts into pursuing fuel cells as potential efficient power generation devices.

The solid-oxide fuel cell (SOFC) is an alternative energy-conversion device that converts the chemical energy stored in fuels (such as H_2 , CO , CH_4) into electricity, through a series of chemical and electrochemical reactions^[4]. SOFC is a complete solid-state device that uses an ion-conducting ceramic material as the electrolyte, which is sandwiched in between two electrodes (anode and cathode, according to Fig. 1.2). SOFCs also produce a significant amount of heat (“byproduct”), which can be harnessed in combined heat and power (CHP) systems to take advantage of this wasted heat. Likewise, the excess of heat can also be used to sustain endothermic reforming reactions of certain hydrocarbons to produce H_2 -enriched gas for effectively fueling the SOFC. More specifically, SOFCs allow the use of a variety of fuels because the anode can serve as an active catalyst for fuel reforming at higher operating temperatures, typically in the range of 650 °C – 1000 °C^[4].

Solid electrolyte materials, as used by modern solid-oxide fuel cells, were not identified until the end of the nineteenth century through the discovery of Walther Nernst^[5] of his so-called “Nernst Mass”². It was a ceramic compound consisting of 85 %-mol ZrO_2 and 15 %-mol Y_2O_3 , and since then this material has been applied as reference for many mixtures of ZrO_2 with rare-earth and alkaline-earth oxides, with the objective of obtaining materials with high ionic conductivity^[6, 7]. Until early 1990’s^[8], ZrO_2 -based materials have remained the mainstream electrolytes since the invention by Nernst more than one hundred years ago.

² Interesting enough, George Westinghouse was the assignor of Nernst’s invention in 1899^[5].

(a)

(b)

(c)

Figure 1.2: general concept of an anode-electrolyte-cathode SOFC (b); Compact stationary SOFC systems fueled by natural gas for distributed power generation: Redox Cube³, 25 kW_e (a); and Bloom Energy Server⁴, 160 kW_e per power module (c).

³ Redox Power Systems website: <http://www.redoxpowersystems.com>.

⁴ Bloom Energy website: <http://www.bloomenergy.com>.

While conventional high-temperature SOFC (HT-SOFC) usually operates between 800 °C and 1000 °C, in the period starting from early 2000's there has been a number of groups^[9] focusing on intermediate (typically operating between 650 °C and 800 °C) and low temperature (below 650 °C) SOFCs (IT-SOFC and LT-SOFC, respectively). Both designs allow wider choices of materials and more cost-effective systems. The lower operating temperature minimizes thermally-driven material degradation and reduces stringent material requirements. Therefore, this line of research tries to bring acceptable lifetime and competitive levelized cost of electricity (LCOE) to SOFC technology⁵.

Due to their high theoretical efficiencies, SOFCs hold a great potential to deliver attractive economics for converting fossil fuels (or renewable fuels, such as ethanol and biogas) into useful forms of energy in a most efficient manner and with minimal environment impact, addressing world's demand for clean and affordable energy. This is especially true when SOFC systems rely on CHP (*i.e.*, bottoming-cycle with conventional thermal engines). In the foreseeable future, SOFCs might find particular application in the niche market of stationary, distributed power generation^[10], and perhaps also as a promising energy storage technology through use of the so-called reversible SOFCs^[11], when they are applied as solid-oxide electrolyzer cells (SOECs) to produce hydrogen gas. However, thus far there are still significant technical challenges inhibiting the full commercialization and wide-scale rollout of SOFC technology.

Despite of the centenary history and the overall multibillion dollars investment over the past fifteen years, SOFCs are still somewhat far off from reaching commercial-grade performance in the market of power sources and achieving subsidy free energy prices (*i.e.*, without requiring leverage subsidies through government policy making to be a competitive technology). There are a number of hindrances that need to be addressed before SOFC become poised for (a realistic) commercial market introduction. For instance^[4, 8, 9]:

- i. There is still lack of knowledge about the fundamental aspects of SOFC operation, which still hides complex and poorly understood processes (from thermodynamics to kinetic phenomena) stemming from different and overlapping scientific domains.
- ii. High overall product cost (high capital expenditure), regarding both manufacturing and balance-of-plant (BOP) related costs. High temperature operation unequivocally requires exceptional properties of materials and assembled modules.
- iii. Not enough attention has been drawn to problems of SOFC insufficient long term durability and reliability, with direct impact on fixed and variable maintenance costs, as well as on the average capacity factor of SOFC power generation systems.

⁵ LCOE represents the per-kilowatt hour cost (in real dollars) of building and operating a power plant over an assumed financial life and duty cycle.

1.3.2 SOFC Components and Functionality

There are four basic functional elements in a SOFC: electrolyte, cathode, anode, and interconnect. The material for these components is typically ceramics, metals, or a cermet (see also §§1.3.4). More generally, a SOFC consists of two porous electrodes separated by a dense, oxide ion-conducting, ceramic electrolyte (see Fig. 1.3). These three layers when stacked together are often referred to as MEA (membrane-electrode assembly) or PEN (Positive-electrode/Electrolyte/Negative-electrode). When the PEN and interconnects are coassembled they form a single cell, which is typically only a few millimeters thick^[7, 8]. The ceramics used in SOFCs do not become ionically active until it reaches high temperatures⁶.

The structure of the electrode is porous to ensure that both the electrolyte from one side and gas from the other “can infiltrate it”. This is to give the maximum possible contact between the electrode, the electrolyte, and the gas, given that phase boundary reactions occur at solid/solid/gas interfaces (at the so-called three-phase boundary or TPB). Ideally, feed molecules have to be distributed over the TPB as uniformly as possible and products should be removed without significant difficulties. At this level of description, a SOFC resembles a chemical reactor that needs to be optimized with respect to geometry, materials, and operating conditions^[12].

Figure 1.3: example of a cross-section scheme of ceramic layers in a planar cell (Figure by the author).

The electric current produced by a SOFC scales with the active surface density (*i.e.*, with the reaction regions where gas, electrode, and electrolyte meet). To increase this density, a huge number of catalyst particles are mixed with ionic and electronic conductors to form the functional layers of SOFC^[13, 8]. Thoroughly interconnected pores in the close vicinity of TPB are needed to provide fast delivery of feed gas. However, even in well-engineered layers a large amount of particles might be “disconnected” (*i.e.*, non-percolated) from the electrolyte or located far from the pore and are, therefore, “inactive” for electrochemical reactions.

⁶ In this case, the observed electrical conductivity at high temperatures is attributed to the movement of oxygen vacancies under gradients of oxygen partial pressure^[8].

To understand how the reaction between fuel and oxygen produces an electric current, and where the electrons come from, one needs to consider the separate (half) reactions taking place at each electrode (see Fig. 1.4). Two electrochemical reactions are separated in space by an electrolyte (ionic conductor). For the reaction taking place at the cathode (also known as “air electrode”), oxygen gas molecules react with incoming electrons coming from the outer circuit to form oxide ions (*i.e.*, convert O_2 into O^{2-}), which then migrate across the electrolyte to the anode. At the anode (also known as “fuel electrode”), the fuel supply (H_2 , CO or other hydrocarbon) accepts O^{2-} delivered by the electrolyte and converts it into H_2O (and/or CO_2), liberating electrons which flow from the anode via external load to the cathode. These electrons, flowing via external load, can be harnessed to do useful work (*i.e.*, produce electricity). The cycle then repeats itself as those electrons enter the cathode material.

Figure 1.4: schematics of the working principle of SOFCs. Example of separate anode and cathode reactions, when using hydrogen and carbon monoxide as fuels. Oxygen is usually obtained from air, although it may be fed pure (Figure by the author).

To put it concisely: one of these reactions produces ions (*i.e.*, electrons are added to a chemical species, and likewise electrons are “consumed” by the reaction), in a process defined as oxygen reduction reaction. The other reaction consumes ions (*i.e.*, electrons are removed from a chemical species, and likewise electrons are liberated by the reaction), in a process defined as fuel oxidation reaction. The functionality of an electrolyte is to transport oxygen continuously, and solely in the form of O^{2-} from cathode to anode, for which the overall driving force is the gradient of chemical potential of oxygen^[8] (with the anode having a lower partial pressure of oxygen). Provided that both fuel and oxygen are supplied constantly, continuous electrochemical reactions will steadily generate electricity.

The maximum cell voltage of a typical single SOFC typically reaches up to 1.1 V (or about 0.7 V when drawing a useful amount of electric current), depending on temperature, pressure, oxidant, and fuel consumption^[13]. At such small voltage level, practical engineering applications will not be benefited. Thus, in order to build sufficient high voltage (e.g., 120 V) and power throughput, multiple single cells have to be connected in series and/or parallel with the aid of interconnects. Such collection of SOFCs in series is known as “stack” (see Fig. 1.5). Ideally, interconnects should make connections all over the surface of one cathode to that of the anode of the next cell. Generally, interconnect is ribbed on both sides to allow cross-flow, co-flow, or counter-flow configurations of fuel/air flows (see Fig. 1.5).

Although a good electrical connection must be made between the two electrodes, their respective gas supplies must be strictly separated. That is, SOFC must allow oxygen transport only in the form of O^{2-} (thus not in the form of unreacted O_2). For that to be possible, dense barriers (e.g., electrolytes, interconnects, sealing gaskets, and so forth) between air and fuel streams have to be established to ensure that the two individual half reactions occur in isolation from one another. Ideally, interconnects should be pure electronic conductors and thus oxide-ion insulators. The electrolyte must only allow O^{2-} ions to pass through it (i.e., it must be a pure ionic conductor, ideally). Otherwise, it would be possible for electrons to go across the electrolyte and not via the outer circuit and, in this case, the closed electrical circuit would be lost.

Figure 1.5: example of planar cell configuration (with cross-flow arrangement) in a SOFC stack (Figure by the author).

1.3.3 SOFC Designs

The intent here is to give just a brief overview about more common designs, which should be enough to support the concepts and definitions to be used throughout this dissertation. For a more complete description about “standard” SOFC designs, one should refer to [8, 13]. For newest designs, including the micro tubular single-chamber SOFCs, one should refer to [14].

Modern SOFCs typically consist of a thin electrolyte film and supporting substrates (including porous or channeled dense bodies for gas transport). From a geometric standpoint, the substrate can be made into either tubular or planar shape (see Fig. 1.6). In terms of long-term stability, the tubular concept has demonstrated the best results, while the planar design promises higher power densities^[8]. The planar SOFC may be in the form of a circular disk (“ring type”) fed with fuel from the central axis, or it may be in the form of a rectangle or square plate fed from the edges (see Figure 1.6a). Planar designs can be broken down into electrolyte-supported, electrode-supported, interconnect-supported (metal or ceramic), inactive insulator-supported, or active insulator-supported designs (see Fig. 1.7). SOFC design is intimately related to a particular choice on how to stabilize the cell mechanically.

Figure 1.6: schematics of SOFC geometrical configurations⁷: planar (a); and tubular (b).

Figure 1.7: illustration of three different architectures of cell support types for SOFCs (Figure by the author).

⁷ Pictures reproduced from OSAKA GAS Co. website: <http://www.osakagas.co.jp/en/rd/fuelcell/sofc>.

The selection of cell supporting design must consider additional performance constraints besides mechanical stabilization, such as: chemical stability and thermal expansion compatibility between layers; long-term durability; issues regarding fabrication techniques; voltage losses; and electrochemical catalysis^[8, 13]. For instance, electrolyte resistance is a significant obstacle to further decrease the SOFC operating temperature, thus the manufacturing of thinner electrolytes is of major interest. This can be accomplished by shifting the function of mechanical stabilization from the electrolyte to one of the electrodes. In this concept⁸, existing anode materials tend to be preferred because they exhibit better electrical conductivity. Thus, in this case, no appreciable ohmic losses occur when the electrode thickness is increased (see Fig. 1.8). Moreover, *Ni/YSZ* cermet anodes also have good mechanical stability, allowing larger planar cells to be produced.

Figure 1.8: SEM image of an anode-supported cell (picture reproduced from [14]).

A specific porous structure of thick substrate type is the so-called buffer-layer (also referred to as “anode-barrier”), which will be briefly presented in §§1.3.4.5. Here it is anyway appropriate to add that the use of this type of substrate also implies performance constraints, as already mentioned above for other types of supporting designs. Usually, the buffer-layer is a substrate with high porosity and adequate gas permeability, but the trade-off is that it has much lower effective electrical conductivity^[15]. Therefore, in the particular case that the buffer-layer is also used for mechanical stabilization, the cell should be classified as an insulator-supported design. A final and equally important concept is that of functional layers and composite (functionally graded) electrodes^[16]. The latter is often made by laying down several layers, which allows a gradient of properties ranging from nearly pure electrolyte (e.g., *YSZ*) at the electrolyte surface to almost pure electrode composition at the interconnect contact (see Fig. 1.9).

⁸ Forschungszentrum Jülich began working on this concept around 1993^[14].

Although there are various different designs, SOFC composite electrodes often consist of a “superposition” of at least two layers: (i) one constituted by a pure ion-conducting material; and the other constituted by the electro-catalyst/electron-conducting material (e.g., *LSCM*, *Ni/YSZ*).

Figure 1.9: illustrative example of a composite electrode (cathode, in this case) and its functional layers: current collector layer with thickness l_1 ; and cathode functional layer with thickness l_2 (Figure by the author).

Furthermore, each layer itself can be a mixture of one or more phases, with varying composition of each solid phase along the cell thickness (mixtures such as: pure ion-conductor with a mixed electron-ion-conductor; or a pure ion-conductor with a pure electro-conductor; see Fig. 1.10). For instance, by layering the anode between two slightly different compositions, one nearest the zirconia with less nickel, the other near the gas stream with more nickel, can produce excellent anode properties, both from the catalytic (rapid reactions with the fuel) and conduction (good conduction to the interconnect) points of view^[13].

Figure 1.10: example of a cell with functionally graded electrodes and varying composition (Figure by the author).

SOFC composite electrodes (e.g., *LSM/YSZ* for cathodes; and *Ni/YSZ* for anodes) usually exhibits a superior performance compared to single phase electrodes, since the electrochemically active zone is spread into the electrode’s volume^[17] in the former case. That is, there is a performance increase attributed to an improved contact with the bulk electrolyte as well as to an extended TPB in the composite structure^[13]. An extra substrate may also be added, e.g. on top of the anode, to perform some sort of additional catalytic/protection function (fuel reforming, as in the case of the buffer-layer), as will be succinctly discussed in §§1.3.4.5.

1.3.4 Brief Introduction to SOFC Materials and Fuel Processing

Because the analysis of SOFC materials itself is not within the scope of this work, only an essential overview is given about electrodes and electrolyte materials. The brief introduction that follows should provide a reasonable background to support familiarization with main terminology and to present some key materials characteristics as well. Throughout this dissertation, however, a more in-depth examination of SOFC materials will be done promptly when deemed necessary for complete comprehension of a given topic.

1.3.4.1 Electrolytes

The electrolyte is exposed to both oxidizing (air side) and reducing (fuel side) atmospheres at high temperatures. Such grueling conditions require that, in order to attain successful, long-term operation and maximum electrochemical efficiency, the electrolyte should have the following characteristics^[8]: (i) high ionic conductivity (electrolyte must be a good ion conductor and ideally an electron insulator); (ii) dense structure (electrolyte must be gas tight); (iii) stability (the electrolyte when exposed to both air and fuel, at elevated temperatures, must be chemically stable); and (iv) well-matched thermal expansion coefficient (in a composite material structure, the thermal expansion coefficient must match at the electrolyte/electrode interface to prevent cracking of the joint on thermal changes).

Often used electrolytes materials for SOFCs are nonstoichiometric (*i.e.*, oxygen-deficient) oxides^[18] with low valent element (cations) substitutions, the latter also referred to as acceptor dopants, which create oxygen vacancies (disorder sites) through charge compensation. Historically, SOFCs have been based on electrolytes of zirconia (ZrO_2) doped with the addition of a small percentage of yttria (Y_2O_3). Above the temperature of about 600°C, zirconia becomes a conductor of oxygen ions (O^{2-}), and typically the zirconia-based SOFC operates between 800 °C and 1000 °C. Yttrium-stabilized- ZrO_2 or YSZ (*e.g.*, $Zr_{0.84}Y_{0.16}O_{1.92}$ or, equivalently, 8YSZ) is the most common electrolyte that satisfies the material requirements just described, however there is a wealth of other possibilities, such as acceptor doped CeO_2 and perovskite structure oxides^[8].

Typically, the amount of doping with yttria is of the order of 13-16% by weight (8-10% mol) to give fully stabilized cubic material^[7]. The ability to conduct O^{2-} ions is brought about by the fluorite cubic crystal structure of zirconia in which some of the Zr^{4+} ions are replaced with Y^{3+} ions (when this ion exchange occurs, a number of oxide-ion sites become vacant^[7,8]). The ionic conductivity of YSZ ($0.02\ S\ cm^{-1}$ at 800°C; $0.1\ S\ cm^{-1}$ at 1000 °C) is comparable with that of liquid electrolytes. Although YSZ shows the lowest ionic conductivity (see Fig. 1.11), it remains as one of the few materials that has been demonstrated to provide long-term stability

under real operation conditions^[8]. Different approaches have been attempted in order to apply YSZ in the intermediate-temperature operation. The typical one is to decrease the thickness of YSZ electrolyte and thus minimize the overall ohmic loss. Other approaches include the development of new doped zirconia oxides; however, some of these new materials (e.g., Scandia-doped ZrO_2) often show higher costs and aging issues, making them unsuited (at least at the present time) for commercial application^[14].

Figure 1.11: conductivity as a function of reciprocal temperature for solid-oxide electrolytes.
(figure modified from [4])

1.3.4.2 Anodes (Fuel Electrode)

Composition and microstructure features are critical aspects of anode performance and they should enable the SOFC to meet the following requirements^[13, 8]: (i) an excellent catalyst for the electrochemical oxidation of the fuel; (ii) stable in reducing atmosphere; (iii) good electron conductor; and (iv) have sufficient porosity (20–40%) to allow transport of gas species in (reactants) and out (products) of the TPBs, where the fuel reaction takes place.

The anode is usually a YSZ cermet⁹ in which the metallic component is nickel, thus forming a porous *Ni*-YSZ cermet (see Fig. 1.12a). This *Ni*-YSZ cermet is typically a complex composite-system made of intertwined conductive networks (ionically conducting solid-phase, electronically conducting solid-phase; and gas flow in porous-phase), all of which should ultimately participate in the formation of percolating networks of TPBs (see Fig. 1.12b). The YSZ serves to: (i) inhibit sintering of the *Ni* particles; (ii) provide thermal expansion coefficient comparable to that of the electrolyte; (iii) allow better adhesion of the anode with the

⁹ A cermet is a composite material composed of ceramic (cer) and metallic (met) materials.

electrolyte; and to facilitate the transport of oxygen ions. Nickel is chosen precisely because of its high electronic conductivity and stability under chemically reducing conditions. In a *Ni*-YSZ anode, nickel also has the role of being an electrocatalyst for hydrogen oxidation and a current collector^[13]. It is also a highly active catalyst for the steam reforming reaction of methane^[19], thus the presence of nickel can be used to advantage as a reforming catalyst, making it possible to carry out internal reforming in the SOFC directly (see §§1.3.4.5).

Figure 1.12: 3D reconstruction images showing: (a) solid phases: (b) map of three-phase boundaries (TPB) lines in a SOFC structure, where each color represents a set of contiguous TPBs; and (c) voxel arrangement for better illustrating the geometric definition of the TPB length (3D reconstruction figure (a,b) was reproduced from [347]).

Unluckily, however, *Ni* may also catalyze the formation of filamentous carbon from gaseous hydrocarbons under reducing conditions^[19]. In this case, the anode activity will surely suffer due to formation of the carbon-containing deposits (see §§1.3.4.5). Incorporating oxide-based catalysts (e.g., *Cu/CeO₂*) is an interesting approach^[20] that has been tried to overcome this limitation of *Ni*-based anodes and allow direct utilization of hydrocarbon fuels.

1.3.4.3 Cathodes (Oxygen Electrode)

Composition and microstructure features are also critical aspects of cathode performance and they should enable the SOFC to meet the following requirements^[13]: (i) excellent catalyst for the dissociation of oxygen molecule and oxygen reduction; (ii) stable in oxidizing atmosphere; (iii) good electron conductor; (iv) sufficient porosity (20–40%) to allow transport of gas species in (reactants) and out (products) of the TPB, where the oxygen reaction takes place; (v) the thermal expansion should match with other cell components; and (iv) it should have chemical compatibility and minimum reactivity with the electrolyte with which it comes into contact. Most cathodes are now made from either electronically conducting composite oxides or mixed electron-conducting-ion-conducting (MIEC) ceramics.

The most common cathode material is the strontium-doped lanthanum manganite, e.g. $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$ (LSM), which is often used in composite designs, such as in mixtures of YSZ and LSM (see Fig. 1.9). Mixed conducting perovskites, such as $(La_{0.6}Sr_{0.4})_{0.98}Fe_{0.8}Co_{0.2}O_3$ (LSFC), have been also used as cathode materials. These mixed conducting perovskites, especially the p-type conducting perovskite structures, are particularly attractive because they exhibit mixed ionic and electronic conductivity (see Fig. 1.13). In general, when compared with LSM, these materials offer^[13] higher bulk oxide-ion diffusion rates and exhibit faster oxygen reduction kinetics (including faster surface exchange). The latter aspect is important, considering that the oxygen reduction reaction can constitute a major performance hurdler to the electrochemical performance of SOFCs. The application of multi-layered (functionally graded) cathodes has also been shown to decrease activation losses^[8], especially when adjusting optimum values for both the grain diameter and porosity of cathode at the outer (close to air channel) and inner (close to electrolyte) layers.

Figure 1.13: illustrative idealization of the TPB regions of different SOFC anode materials. Note the extension of the TPB length which is obtained in MIEC materials (figure reproduced from [4]).

1.3.4.5 Fuel Processing

Fuel processing may be defined as the conversion of the raw primary fuel, as delivered to a SOFC system, into the fuel gas that is actually required by the stack (anodes). At least from the point of view of technology feasibility, SOFCs can utilize a wide range of hydrocarbon fuels, provided that these are properly cleaned and reformed into “simpler” fuels such as H_2 and CO ^[4]. Therefore, the main purpose of fuel processing is to convert readily available hydrocarbon fuels into H_2 -rich and/or CO -rich gas (both gases are at times referred to as reformat streams) that can be electrochemically oxidized at the fuel cell anode. The fastest electrochemical reaction at the nickel anode is that of hydrogen gas, but other fuels can react directly with the anode, depending on catalyst composition^[21]. For example, carbon monoxide can also react on Ni/YSZ but it requires a higher overvoltage than hydrogen^[22], meaning that CO electrochemical oxidation rate is relatively slower when compared to that of H_2 .

The fuel may also require some level of purification because fuel impurities (e.g., sulfur) are a common source of damaging mechanism, which ultimately might lead to the total failure of a SOFC^[4]. Sulfur is the most prevalent impurity and can be present in most fuels derived from fossil sources, either by nature or added as odorant. Even lower levels of sulfur (in the order of ppm_v), such as those found in odorants used in natural gas for leak detection), are damaging to SOFC nickel anodes^[4] given that sulfur and sulfur-compounds are known to adsorb and cause a loss in the electrode performance^[23]. There are two approaches to tackle this problem: adding a sulfur absorber to the fuel processing unit (see Fig. 1.14); and/or using anode metals that are less likely to be negatively affected by sulfur.

Figure 1.14: illustrative example of a SOFC/GT combined cycle system, incorporating a desulfurizer unit to purify the fuel upstream of SOFC anodes (figure reproduced from [4]).

The requirements and complexity of the fuel processing step depends largely on both fuel cell type and raw fuel. The nickel content in the anode of SOFCs means that internal reforming reactions can be carried out directly (internally) in porous anodes, and this is to a great advantage in minimizing the overall system complexity and total costs^[4]. The high operation temperature not only provides waste heat exhaust, but it also effectively activates the processes of reforming in the presence of suitable catalysts (such as nickel-based materials). The electrochemical oxidation of fuels gives off excess heat that can be utilized by the highly endothermic steam and/or dry reforming reactions simultaneously taking place, which makes internal on-cell reformation possible, precluding the need for external reformer and allowing chemical integration with the main products (e.g., H_2O/CO_2) originated from electrochemical reactions. This possibility has led to various internal reforming concepts on the account of SOFC high operating temperature. In one of these concepts, fuel reforming occurs when steam is added to hydrocarbon fuel stream (typically at a ratio of 3 parts steam to 1 part fuel) in SOFCs with the so-called direct internal reforming or DIR design^[4, 13]; or, alternatively, when using virtually dry fuels (without the need of adding steam to the inlet fuel stream) in SOFCs that operate with gradual catalytic reforming^[24].

Unfortunately, however, the main advantages of DIR-SOFCs can be completely offset by the occurrence of “anode coking” (i.e., carbon deposition), which can render the SOFC permanently non-functional after short time of operation^[25]. Thus, a major roadblock to long-term stability of DIR-SOFCs operating on methane and other hydrocarbon fuels is the anodic carbon deposition. Nickel-based anodes have the propensity to coke^[8], that is, to become coated (and blocked) with a carbon layer on reacting with dry fuels such as pure methane. From this point of view, nickel-based catalysts may not be a suitable choice for DIR applications, if care is not taken to ensure a proper fuel/steam ratio before the fuel mixture reaches the anode active layer. There is, however, an alternative cell design that tries to tackle some of the stability limitations that are typical of standard *Ni*-cermets. In contrast to traditional SOFC designs, in which *Ni*-based anodes act as the only effective catalyst for internal reforming, this alternative design suggests the use of a barrier-layer architecture. In other words, “a barrier” is done by the addition of either a thin catalyst layer^[24, 26, 27] or thick inert layer^[28] between the anode and fuel channel (see Fig. 1.15).

Both chemically inert and catalytic anode barrier layers are found to offer advantages when compared to conventional techniques, because they permit a more complete reforming and deposit-free operation (i.e., they process the fuel and protect the anode) by enhancing stability and locally slowing catalytic endothermic reforming reactions. In terms of stability, the barrier hinders the flux of fuel into the electro-catalytically active region and likewise hinders

the flux of CO_2/H_2O from the anode to fuel channel. Accordingly, the gas-phase composition in contact with Ni can be maintained in a coke-free thermodynamic region^[8].

Figure 1.15: design with barrier-layer, where the catalytic case is shown (a); schematics of how reactant and product concentrations are expected to vary spatially during operation without (b) and with (c) catalytic barrier layers (Figure by the author).

1.4 Mathematical Modeling of Solid-Oxide Fuel Cells (SOFCs)

The sections that follow are intended to provide a summary of the main topics to be addressed in this work. Although this summary was not elaborated in a systematic way, it is expected nonetheless that the given information should facilitate the future comprehension of these topics and how they interrelate to one another (see Fig. 1.16) in the next chapters.

Figure 1.16: main subject areas underlying the mathematical modeling of SOFCs in this work.

1.4.1 Modeling on the Single-Cell Scale

Although much of the modeling approaches that will be discussed in this work could be used with different SOFC configurations, the focus herein is on one specific design: button-type SOFC^[29, 30] with a normally impinging circular jet flow configuration in both air-side and fuel-side compartments (gas channels), as illustrated on figures 1.17 and 1.18. Single button-cells play a major role in the development and evaluation of new SOFC materials and PEN architectures^[13]. These single-cell tests are useful to determine the cell performance under ideal conditions, where gold or platinum are often used to make excellent current contact with the electrodes (though there still are contact issues that might severely bias the experimental readout^[29]). The primary purpose of button-cell testing is to provide a method of assessing the effects of changes in cell design, component materials, and fabrication processes.

While it is always desirable to obtain accurate results, the usual outcome of screening tests using button cells is comparative in nature. In other words, many experimenters use button cell testing as a relative rather than absolute test method. By defining a reference polarization curve or impedance spectrum for well-defined materials and operating conditions, the changes relative to the reference condition are determined and interpreted^[30]. However, despite this seemingly simple comparison methodology, it is important to recognize that broader implications can be inferred from button-cell results^[13, 29]. According to Fig. 1.17, most button-cell tests are performed in temperature-controlled furnaces, where the anode/electrolyte/cathode (PEN) is held concentrically between other tubes, which are made of either glass or ceramic materials.

Typically, PENs are small circular cells of one to five centimeters in diameter that are bounded to tubular fixtures. All these tubes must be sealed hermetically against the PEN disc before the assembly is positioned within the furnace. Reducing and oxidizing gases are supplied to either side (anode and cathode sides, respectively) of the PEN via much thinner inner feeding tubes¹⁰. For example, in Fig. 1.17b a fuel mixture flows from top to bottom in the fuel channel at the top, and is transported into the pores of the anode-barrier. In the buffer-layer and anode the fuel mixture undergo chemical reaction on catalyst surfaces and one or more species, which can be either initially present or produced *in situ*, may then be electrochemically oxidized on reaching the anode active layer near the dense electrolyte. For each experimental run, the porosity, particle sizes, pore sizes, and the chemical composition of electrode layers may, in principle, all vary along the cell thickness in order to acquire different types of experimental information.

¹⁰ In button-cell experiments, the cathode side is usually exposed to air that may simply be the furnace air or it may be supplied via a feed tube. The latter case is shown on figures 1.17 and 1.18.

Figure 1.17: schematic representation of button-cell testing assembly (a); two-dimensional schematic view of the experimental testing section and computational modeling domain commonly used for a DIR-SOFC model simulation (b); actual photo of a test bench¹¹, which is typical of button-cell experiments (c). (Figure by the author).

¹¹ From the Laboratory of Prof. Sossina Haile, California Institute of Technology.

Figure 1.18: schematic representation of different button-cell designs: both fuel and air channels have the same configuration^[31]; (b) and the air channel with a finite-gap stagnation flow^[32].

Button-cells inherit their main characteristics from a wider group of flow reactors, the so-called stagnation flow reactors (SFRs). Stagnation flows represent a very important class of flow configurations^[33] wherein the transport equations often reduce to a system of ordinary differential equations (ODEs) describing boundary-value problems. Some of these flows have great practical value in industrial applications, such as in chemical-vapor-deposition (CVD) reactors^[33]. They are also widely used in catalytic combustion research^[34].

Stagnation flows may be seen as a particular case of normally impinging circular jets in confined spaces and, depending on the problem's geometrical dimensions and fluid flow parameters, different flow similarity reductions (either complete or incomplete) are possible^[35, 36]. A peculiar feature of SFRs is that the phenomena under study usually take place within a thin viscous region adjacent to a solid surface, which usually plays a catalytic role. Thus, SFRs are often employed to study heterogeneous catalysis problems under “ideal conditions”. The idealization aspect of SFRs refers to the condition that the processes occurring at the solid surface should not be influenced (limited) by upstream conditions (the outer flow region). More generally, in SFRs the result of the interaction between the outer flow region and boundary-layer is assumed to be well known (“controlled and resolved”), thus any effects stemming from this interaction might be seamlessly separated from, for example, the intrinsic reactivity of surface catalysis (see §§4.10).

There is a large body of experimental data on SOFC button-cell experiments running on fuels such as H_2 , CH_4 , C_2H_5OH , and higher HCs. However, although the existing setups for button-cell testing share many common characteristics, different research groups follow different practices in testing cells and reporting experimental data. At the moment of this

writing, there are still no strictly standardized single-cell testing procedures providing forethought and criteria for conducting such tests, though there were attempts in this direction^[37]. The careful consideration of what is necessary to successfully test button-cells can often bring increased awareness about otherwise “inexplicable” experimental results. Moreover, many underpinning mathematical models that depict the behavior of PEN architectures are usually developed and validated with button-cell experiments. It is therefore of paramount importance to understand, in an unambiguous manner, the influence of experimental setup and operating conditions on measured cell performance. Numerical investigation of cell performance should ensure the use of physically consistent model parameters to explain the experimental outcome.

As mentioned above, button-cell testing permits comparative appraisal based on changes of design, materials, and operating conditions. In this regard, there is a certain degree of “flexibility” only insofar as the model parameters can be adjusted to fit experimental data. However, this flexibility can be elusive, especially if contentious conclusions arise from the comparison between model predictions and experimental results. Such situation can indeed occur if, for instance:

- If a given mathematical model (and its underlying assumptions) is unfit for the purpose of credibly describing the physical reality of the experiment. In this case, it is not uncommon the use of inconsistent parameters solely for the intent of “best fitting” the experimental dataset, and as a way to compensate for other sources of error (*i.e.*, as in a false correction), thus disregarding the physical pertinence of the model itself.
- The test itself was not well thought out, meaning that “meaningless” results can follow from either improper testing procedures or wrong assumptions about the actual experimental conditions. Sometimes there is a nuance on how to differentiate between these factors.

Due to either of the causes just mentioned above, conclusions tend to lessen in practical value and, ultimately, the objective comparison between model and experiment is impaired. An examination concerning these aspects must be performed, including the scrutiny of different reactor models (*e.g.*, plug-flow, finite-gap stagnation flow, and flow between parallel discs) and the evaluation of possible sources of experimental bias, such as seal leakage during cell tests. It is important to mention that part of the works in the literature that will be reviewed in **Chapter 4** has employed different experimental setups for the gas channel (planar cells with parallel flow, for example). In spite of that, the remarks made above about button-cell testing remain valid in respect to the importance of understanding the influence of experimental setup on the *de facto* measured cell performance.

1.4.2 Concepts on Multiscale Modeling and Multiphysics Simulation

Dominant forces that influence micro-scale components, such as the PEN in SOFC systems, are peculiarly different from those that influence their conventional-scale (macroscopic) counterparts. This is because the size of a physical system bears a significant influence on the natural processes that dictate the behavior of that system, *i.e.* variance in scale might lead to sensible differences in transport mechanisms. For example, large-scale systems are influenced by inertial effects to a greater extent than small-scale systems, while the latter is influenced greatly by surface effects. In many scientific disciplines, this concept of interrelating scales and physical phenomena is commonly called “physics of scaling laws” [38].

During the development stage of a mathematical model, an approach is usually specialized toward particular phenomenon and scale. This screening strategy is largely due to the need to rationalize the overall goal of modeling activities, when computational cost and theoretical uncertainty must be both quantified and balanced (via trade-offs) in order to accurately and feasibly describe the critical processes responsible for SOFC performance. Nonetheless, the simulation of SOFC systems is a problem that incorporates important features from multiple physical scales^[2]. Therefore, in principle, a number of different and simultaneous physicochemical processes (“multiphysics”) that take place over a wide range of spatio-temporal scales (“multiscale”) have to be acknowledged. When a detailed understanding of the relevant processes at a given scale is required, one should refer to more specialized models that treat the details of single parts of the SOFC (e.g., models specifically developed and validated for the “PEN or single-cell scale”). Even so, electrode-level phenomena still entail a considerable challenge for traditional (“single-scale” or monoscale) modeling approaches, because transport and thermodynamic processes occurring in the PEN are also strongly, and often nonlinearly, coupled over various length and time scales^[3]. Furthermore, this coupling effect can manifest itself as a dominant influence of the microscale physical-chemistry over the macroscopic behavior of SOFC and, in this case, such intimate degree of interdependence should not be undervalued.

To cope with the multiscale character of the problem at hand, the existing SOFC modeling techniques (see Fig. 1.19) range from atomistic to system-scale applications^[1, 2], likewise multiscale model methods^[39] range from quantum to classical (field) mechanical theories. For the most part, multiscale modeling intend to predict material properties and/or system behavior on one scale using information, e.g. models and/or experimental data, from different scales^[40], a concept which is usually referred to as “scale linking” or “scale bridging”. According to Fig. 1.19, on each distinct scale, a specific modeling technique can be used to

describe the system, as for instance: (i) scale of quantum mechanical models (information about electrons is included); (ii) scale of molecular dynamics models (information about individual atoms and/or molecules is included); (iii) mesoscale (information about groups of atoms and/or molecules is included); (iv) and the scale of continuum models¹², also known as macroscopic, coarse-grained or conventional-scale models (device-level or system-level information is included).

Figure 1.19: overview of the multiscale modeling approach¹³: illustrative scheme of time and length scales involved in modeling SOFCs (figure modified from [2]).

The use or not-use of multiscale modeling methods depends heavily on whether and how they can be applied in practice and also what the expected benefits are in comparison to other modeling approaches. Briefly, one may distinguish two main cases:

- i. The phenomenon of interest is dominated by processes occurring on different characteristic scales. That is, the phenomenon presents substantial spatial and time heterogeneity on these scales and, therefore, such heterogeneities must be evaluated by theoretical (“more detailed”) models in order to produce useful simulation results. In this case, therefore, multi-scale resolution is an intrinsic requirement to assess the SOFC performance.

¹² Here one must bear in mind the distinction between definitions of continuum from mathematics (e.g., continuum hypothesis, linear continuum, continuum theory of topology) and that from continuum mechanics^[41].

¹³ Strictly speaking, neither the FVM nor FME is tied to any specific scale restriction, when they are viewed as purely discretization schemes. Thus, these methods are not necessarily applied only to macroscale-continuum formulations of governing equations. For instance, the FVM has been used^[42, 43] as the method for solving the discrete formulation of Lattice-Boltzmann Equation (LBE). However, the application of the traditional forms of FVM and FEM in complex geometries might be not suitable for multiphysics numerical simulations, such as in those geometries resulting from the detailed (“structure-resolved”) description of porous media on the nanoscopic or mesoscopic length scale.

- ii. The interest consists in predicting material properties or system behavior based on the knowledge of more elementary processes and/or fundamental properties, even though physical scaling effects do not need to be accounted for explicitly to produce useful results on the scale of interest. For example: one wishes to investigate what is the influence of the grain size distribution (i.e., a subscale influence) of an ionic phase on the effective conductivity of a given electrode material. However, all that would be required to calculate this effective value on the macroscale is the phase's temperature, through the use of a suitable single-scale (lumped parameter) model. Thus, in this case, subscale resolution is not mandatory to assess SOFC macroscale performance. No doubt this is simply a matter of research convenience.

In both cases above, accounting for the interactions from multiple levels turns to be a critical ability in understanding the phenomenology that one is particularly interested on and which is observed from some deliberately chosen scale. It should be manifest, however, that there is an inherent level of subjectivity when deciding whether to use high-fidelity microscopic models or to apply coarse-graining of those models^[40]. Depending on the overall goal of the numerical simulation, in some situations one can apply “one-dimensional” or even “zero-dimensional” models to complex problems and still succeed in their application, provided that enough lumped parameters are available “to fit” the experimental behavior. It must be equally evident that in this situation there is loss of information, lack of generality, and also possible physical inconsistencies at the expense of simulation pragmatism. On the other hand, the coarse-graining can deprive the model of its complex scale-to-scale interaction on which the main physical-chemical behavior depends for a proper description. In this case, the accuracy of lower-dimensional calculation models can become a fallacy. Moreover, these models often become strongly dependent on rather “random best fitting” and “best guess” averaging procedures, with resulting parameters that are disproved of physical consistency.

Much depends on the purpose of the simulation and what type of problem is being tackled. For example, the dynamic and predictive control modeling of SOFCs on a system-level^[44] is computationally prohibitive, if detailed descriptions of all parts of the fuel cell are to be included. Thus, rationalization of computational effort and accuracy requirements form the basis of the modeling strategy. The decision-making often involves the selection of a “fit for purpose” modeling technique: a model should be reasonably accurate and detailed enough to capture characteristics that are deemed important to the numerical study; on the other hand, the selected model should, ideally, require a much lower computational effort than that required by atomistic-level models.

1.4.2.1 Constitutive Information for Multiscale Modeling

Once the superstructure of the modeling approach (*i.e.*, its governing equations) has been established, a critical step is to define reliable and accurate constitutive equations (*i.e.*, closure relations) for the materials involved (*e.g.*, gas species and porous solids). These relations are usually expressed in terms of the various parameters appearing in governing equations (“balance laws”) and their evaluation can be performed through theoretical constitutive equations of material models, using experimentally fitted values, or both. The type and number of constitutive terms that will require prescription depends solely upon what modeling approach has been selected. Thus, here one faces a subtle “back and forth trade-off”, but an important one.

If one selects a model for which a “mathematical closure” relation is necessary, such relation must be somehow known upfront to guarantee self-consistency of the chosen modeling technique. Moreover, if this specific closure greatly affects the results as predicted by the model, then it is of utmost importance to have a closure relation that can be reliably and accurately evaluated. If this is not possible, one should strive to identify another (more) appropriate modeling superstructure. Thus, ascertaining whether a property can or cannot be evaluated interferes in the screening process of modeling techniques. More often than not, the more detailed the model the greater the number of properties that will need proper mathematical description. In general, the extent of one's knowledge about the properties of a system restrains the amount of details that is possible to accrue from numerical simulations.

Transport and thermodynamic properties are a necessary part of physical models, inasmuch as characterizing the molecular transport in multicomponent-multiphase mixtures requires, for example, the evaluation of viscosities and diffusion coefficients. The characterization of molecular transport should be underlined by the discussion about the thermodynamic formalism (*i.e.*, constitutive relations) that actually supports the evaluation of those material-related properties. That is, there should be some analysis on the adopted macroscale mixture theory and whether or not heterogeneous systems^[45] have been properly considered in this theory. However, these formalisms are often tacitly and uncritically adopted in the SOFC literature. This is an important topic, because a given thermodynamic theory might not be consistent in the wide sense of a microscopic theory of processes that occur in systems that are not in statistical equilibrium. In these situations, kinetic properties are more closely related to the nature of microscopic interactions of a particular phenomenon^[46] than to that of the “averaged” macroscopic behavior. Nevertheless, considering what has been argued in §§1.1, this type of discussion (“analysis of general thermodynamic formalisms”) is beyond the scope of this work.

Finally, it is worth to mention that in the case of closure relations that are based on experimentally measured information, property data furnished by “conventional” (macroscale) methods are integral values over some *a priori* characteristic time and length scales (inherent to the experimental technique used). That is, the available data already represent averaged values in some sense. This fact may or may not limit the usage of this experimental information in fine-scale models whose aim is to solve problems over significantly distinct time and length scales. In other words, there may be an intractable “lumping effect” that can render the simulation results unreliable, if the intrinsic averaging of fine-scale models (when these are integrated over the computational domain) does not lead to the same natural average of the experimental test from which property data was obtained.

1.4.3 Mass Transfer in Chemically Reacting Gas Flows

Although this work addresses a specific problem (e.g., gas transport in SOFCs), its theme belongs to a wide field of research, which is the modeling of transport processes in porous medium systems^[47, 48, 49, 50, 51, 52, 53, 54]. In this field, certain subject areas play a major role, namely: (i) factors related to material (structure and properties) characterization of porous domains; (ii) dynamics of fluids in the percolated voids of porous spaces, including multicomponent physical kinetics and thermodynamics aspects; and (iii) the heterogeneous (metal-catalyzed) chemical-electrochemical reactions on pore-wall surface. The modeling of transport processes within porous catalysts entails a multitude of problems, the majority of them of severe complexity and still under intense debate in the literature^[55, 56]. Most notably, the theoretical limitations of the phenomenological modeling techniques commonly applied to describe the intrinsic multiscale nature of surface-catalyzed phenomena^[55, 57].

To some extent, the turmoil and uncertainty found in the literature, concerning both the experimental and theoretical aspects of transport phenomena in porous media, make impossible to extract a theory of the comprehensiveness that is desired. Moreover, it is often arduous to disentangle hard distinctions from elusive research findings, where the latter might be merely an accurate measure of a prevailing bias^[58]. In the specific case of this work, however, this is not a complete fair depiction of the state of affairs as this is not what essentially prevents one from obtaining a consistent mathematical framework. What one should consider of great difficult is not the lack of satisfactory theories, but rather the widespread ambiguities, misunderstandings, and confusion stemming from the derivation and application of some of the existing (and not usually regarded as well-established) transport phenomena models. Confidence in the use of these models is probably undermined primarily when: (i) their physical assumptions are not properly acknowledged; (ii) their results are

claimed more certain than they really are; and (iii) when they are assumed to have far-reaching applicability, when forcibly they have not. It is necessary therefore to recognize that the model should be verified considering its real context of application. For example, the underlying theory for evaluating the problem of multicomponent diffusion in the free (unconstrained or “bulk”) gas volume can be dramatically different when wall effects are (or should be) taken under consideration, as it is the case for diffusional transport in tight porous media. Similar statements can be drawn on the basis of the influences from chemical reactions, adsorption/desorption, viscous shear, and gas rarefaction on diffusion mechanisms. To rightly solve the problem of multicomponent transport, a consistent and all-encompassing (extended) thermodynamic basis is needful to derive phenomenological equations that are able to capture the complexities of multicomponent transport^[59, 60, 61].

There is a long-time state of confusion in the area of multicomponent transport in capillaries and pores, when macroscale phenomenological frameworks are applied. Many models and theories have been devised based on a large number of simple approximations, such as the “Bosanquet formula”^[62], for which it was stated that the linear momentum conservation was, allegedly, the basis for the derivations. However, nowhere the fluid shear appeared. Present mass transport theories often used by chemical engineers, stemming from the statistical-mechanics developments of Chapman–Enskog, Zhdanov–Kagan–Sazykin, and Bearman–Kirkwood apply only to systems with low shear (e.g., see §§3.6). These theories are not able to satisfactorily describe gaseous counter-diffusion in small pores as well. The linear irreversible thermodynamics theory by de Groot–Mazur and Hirschfelder–Curtiss–Bird also demonstrates several shortcomings. Some authors also developed models based on forceful erroneous steps in an attempt to repair the faults of their starting equation, e.g., as it is the case of the well-known Dusty Gas Model^[63, 50].

It is clear, therefore, that a rigorous understanding of the complete set of wall-constrained governing equations of gas transport would be crucial to analyze the problems addressed in this dissertation. For instance, it seems of utmost importance the need for a better and more clearly identifiable justification for the origin of the pressure gradient terms in the macroscale Maxwell–Stefan formalism^[64, 65]. To fail in doing so can lead to “unnoticed consequences” that are as formidable as the lack of mass conservation, as it is, in fact, the case of some models found in the SOFC literature^[66]. Unfortunately, there is a prevailing trend in the development of purely macroscopic phenomenologies that considers that mathematical formalisms, which are needed to describe the mixed-gas transport behavior, are much the same for all types of porous media. Such generalization cannot hold on well-founded physicochemical principles, especially due to the interplay of both multiscale and multiphysics

occurring in these systems. Inherent limitations of the linear non-equilibrium thermodynamics, on which many phenomenological frameworks are based, have greatly contributed to such misconceptions. The apparent absence of due criticism of such models in the literature seems to amount to acceptance but the relevant microscopic characteristics of interrelated transport phenomena (e.g., mass transfer, wall effects, chemical reactions) can surely impact the veracity of these models at the macroscopic continuum.

An analysis of mass transport should be performed to rule out inconsistencies or, which is the same, to establish a well-defined mathematical description of the transport phenomena that could significantly affect critical physicochemical processes. Mass transport constitutes one of the “building blocks” (see Fig. 1.16) that needs to be analyzed in its particularities and then, subsequently, in its interactions with other scientific disciplines (see Fig. 1.20 and Fig. 1.21). It seems reasonably logical that specific inaccuracies from one block can propagate to the others and, depending on the number and relative influence of such “inconsistencies”, the resulting variants of “error of judgment” can become baffling. In other words, the fact that many sources of error can have the same “intractable weight” can render the overall analysis incredible. Thus, when trying to make a sizeable evaluation of potential inconsistencies one expects to lend credence to conclusions of this work and make them theoretically tractable.

Although the focus of this work is to describe transport processes taking place in the gas-phase (“multicomponent gas flow in SOFC porous layers”), it would be impossible to have a well-posed physical problem without also examining, to some extent, aspects related to electrochemical reactions and charge transport. Even so, “for the sake of feasibility” and not to overwhelm this work with endless accounts of sub models, these other aspects will be treated as “black-boxes” as much as possible. The specific mathematical form accounting the interactions between gas-phase transport and electrochemical reactions (interfacial phenomena) depends on the coarse-graining of the models considered. Regardless of the scale of description, interfacial phenomena always will be represented in some form of mathematical abstraction (local microscale balances, boundary conditions, “pseudo-heterogeneous” volumetric source terms, and so forth). These interface entities, whichever their explicit form are, will always have relevant impact on the modeling of gas-phase transport. However, no in-depth analysis will be made about them in this work, which would include the known limitations of the mean-field approximation when it is used to describe nanoscale-driven heterogeneous catalysis.

Figure 1.20: illustrative scheme that reveals some of the existing interactions between mass transfer and chemical reactions, in the mathematical modeling of a SOFC. Question marks represent possible sources of inaccuracy (Figure by the author).

Figure 1.21: schematics of mass transfer models and their imbricated physicochemical phenomena (Figure by the author).

1.4.4 Electrochemical System

Even though the electrochemistry is the “heart and soul” of any fuel cell device^[67, 68], it was intentionally decided to not pursue a thorough review of electrochemical modeling in this work, and thus avoiding any rigorous or extended presentation about the fundamental concepts of electrochemical engineering. The reason being that such task would require tremendous effort and thus consume much time that could be otherwise spent on the cornerstone issues that this dissertation really aims to address, namely: mass and momentum transport modeling in the gas-phase. To clarify further about this scope delimitation, here follows a brief reasoning.

A number of electrochemical processes (e.g., charge transport, electrochemical kinetics, and thermal effects in non-isothermal systems) has an additional “encumbrance” when they are compared to other research topics considered in this work. Several fundamental aspects of SOFC operation still involve not very well understood physicochemical phenomena, thus many questions remain on the exact electrochemistry theory that could describe such aspects. In other words, there is no unarguable consensus on the mechanisms and phenomenology underlying the design of these electrochemical systems. For instance, charge transfer kinetics remains as one of the least understood aspects of the electrochemistry^[69, 67, 13, 70, 71, 72] of solid state devices. In this way, the attempt of pursuing fully credible SOFC models at various levels of detail, from continuum-level electrochemistry approach (aimed at macroscopic simulations) to “microscale” studies using structured-resolved/molecular-level approaches, seems unpractical at the present time. Therefore, considering the scope limitations of the present work and the available research knowledge, the author opted to dedicate efforts to some key aspects of SOFC modeling, which are, on some level, related to concentration polarization processes.

Chapter 2

ON THE PHYSICAL CHEMISTRY OF SOFCs

2.1 Fuel Cell Equilibrium Thermodynamics

At this point it is worth to clarify the reasons for including a small and yet relevant excerpt related to the “black-box” thermodynamics of a fuel cell (see Fig. 1.2a). As will be made clear latter on, many of the mathematical models used to evaluate the so-called “concentration-induced losses” are based on thermostatics considerations. Even though these models may take a further Gibbsian approach (*i.e.*, in the sense that there is a more detailed physicochemical look inside the “black-box” thermodynamic system), it should remain apparent that there is an underlying classical (global) equilibrium thermodynamics framework linking some of the terms/relations that appear in such simplified models. In other words, one must emphasize that the derivation of these terms/relations implies, at least at their natural origin, a global state of exact balance for the potentials, or driving forces, within the macroscopic system. Thus, any “extrapolation” of such terms/relations, when used “unnaturally” in a local form of balance laws (now tacitly considering the state of the system to be non-uniform-locally-varying in presence of dissipative thermodynamic fluxes), must be duly scrutinized at the pertinent time.

The following discussions are restricted to electrodes in equilibrium with both the electrolyte phase and adjacent gas phase. In this phase equilibria, the cell potential can be expressed in terms of the electrochemical potential of chemical species present on the electrode surface and also in the gas that fills the voids of porous structures^[67]. The condition of phase equilibrium precludes the passage of anything but an infinitesimal electric current. Moreover, it is tacitly assumed the inexistence of other spontaneous chemical reactions that do not require a net current to occur. Equilibrium does also imply macroscopic homogeneity in a given phase, in the sense that local migrational equilibrium^[73] does not take place anywhere within that phase.

2.1.1 The Open Circuit Voltage (OCV)

For illustrative purposes, consider the basic (global) electrochemical reaction for the archetype hydrogen/oxygen SOFC:

The Gibbs energy is a relevant quantity in the case of fuel cells (or any electrochemical device for that matter), for which it may be defined as the “energy available to do useful external work, but neglecting any work done by changes in pressure or volume”^[4]. In this case, the “useful work” involves moving electrons round an external circuit and any work done by change in volume/pressure between the input and output is not harnessed by the fuel cell itself. In other words, Gibbs energy is a quantity that can be directly associated with the electrochemical energy conversion in a SOFC. Thus, considering both reactants and products under the same constant p and T , one can express reaction (2.1) as:

$$\Delta_r G(p, T) = \Delta_f G(p, T) = G_{f|H_2O} - \left(G_{f|H_2} + \frac{1}{2} G_{f|O_2} \right) \quad (2.2)$$

In general, the Gibbs energy of formation is a function of temperature and state (liquid or gas), and, in the specific case of a fuel cell, its value is negative ($\Delta_r G < 0$), meaning that energy is released in the transformation given by reaction (2.1). If there are “no additional losses” in the fuel cell (*i.e.*, the process is reversible and the entropy change is only due to a reversible chemical reaction to create new water molecules), then all the Gibbs energy can be converted into electrical energy.

The basic operation of a SOFC was depicted in **Chapter 1**, wherein it was shown that, for a pure hydrogen-fueled cell, two electrons pass round the external circuit for each water molecule produced and for each molecule of hydrogen consumed. Thus, for one mole of hydrogen used, $2\mathcal{N}_a$ electrons pass round the external circuit. If e^- is the charge on one electron, then the total charge flow is:

$$-2\mathcal{N}_a e^- = -2F \text{ [coulombs]} \quad (2.3)$$

Where $\mathcal{F}$ is the Faraday constant ($\mathcal{F} \cong 96485 \text{ C mol}^{-1}$). If E is the fuel cell voltage, then the reversible electrical work done moving this charge round the circuit is

$$\text{electrical work done} = \oint (Q_e \nabla \Phi(\mathbf{r})) \cdot d\mathbf{r} = -2FE \text{ [joules]} \quad (2.4)$$

Where Q_e is the charge being moved (and on which coulombic forces act); $d\mathbf{r}$ is the charge displacement; Φ is the electrostatic potential (voltage) field calculated at some point $\mathbf{r}$; If the process is reversible, this electrical work will be equal to the Gibbs energy released $\Delta_r G$. Thus^[4],

$$\Delta_r G = -2 \mathcal{F} E_{rev} \Rightarrow E_{rev} = \frac{-\Delta_r G}{2 \mathcal{F}} \quad (2.5)$$

This equation gives the electromotive force (EMF) or reversible voltage (E_{rev}) of a hydrogen SOFC. This is the voltage drop between the anode and the cathode under open-circuit conditions (*i.e.*, under zero net current condition), with the electrochemical potential of oxide ions equilibrated through the oxide-ion conducting electrolyte layer. Equation (2.5), derived for the reversible open-circuit voltage (OCV) of a hydrogen/oxygen SOFC, can be applied to other reactions, by generalizing it to any number z_e of electrons per mole of fuel,

$$E_{rev} = \frac{-\Delta_r G}{z_e \mathcal{F}} \quad (2.6)$$

2.1.2 Fuel Cell Efficiency

The way to define the efficiency of fuel cell devices is not unique. Thus, statements such as “the maximum possible efficiency” of a fuel cell can mean different things, depending on the different constraints that are imposed to a given engineering problem. For instance, if there were no irreversibilities then all Gibbs energy would be converted into electrical energy and, if the reference is taken to be the Gibbs energy itself, the efficiency could be said to be 100%. Evidently, this is not a helpful definition for the efficiency when only considering reversible transformations. Since fuel cells use feed materials that are also commonly burnt to release their energy (*e.g.*, as in combustion-based processes), and to get a good comparison with these other fuel-using systems, the efficiency of the fuel cell is often defined as^[4, 8, 68]

$$\frac{\text{electrical energy produced per mole of fuel}}{-\Delta_r H} \quad (2.7)$$

Where $\Delta_r H$ is the heat that would be released by burning the fuel. More precisely, in this case, it is the change in the enthalpy of the electrochemical reaction. However, even this definition is not free of ambiguities, as there are two different values that can be attributed to $\Delta_r H$, the difference being the enthalpy of vaporization of water, that is, whether the product water was considered to be condensed back to liquid or not. Thus an efficiency value should mention whether it relates to the higher heating value (HHV) or lower heating value (LHV) of the fuel. Because the SOFC operates at high temperatures (and at moderated to low operating pressures, *i.e.* ≤ 5 atm), the water is assumed to be in gas phase.

All in all, based on the above definition one can see that there is a limit to the cell efficiency, even if the maximum electrical energy available is equal to the change in Gibbs energy, in this case

$$\epsilon_{max} = \frac{\Delta_r G}{\Delta_r H} \quad (2.8)$$

This maximum efficiency (ϵ_{max}) limit is usually referred to as the “thermodynamic efficiency” of a fuel cell, and is also a function of the temperature, and the state of reactants and products. This result of choosing $\Delta_r H$ among several possible alternatives of “energy reference” is also grounded on thermodynamic arguments. For a reaction running under constant pressure and temperature, the following well-known thermodynamic relation is shown to hold^[74]:

$$\Delta_r H = T \Delta_r S + \Delta_r G \quad (2.9)$$

For a hydrogen fuel cell $\Delta_r H < 0$, $\Delta_r S < 0$, and $\Delta_r G < 0$. Thus $|\Delta_r H| > |\Delta_r G|$ and $\epsilon_{max} < 1$. Equation (2.9) can be viewed as a global thermodynamic limitation of the electrochemical energy conversion process. Equation (2.8) may be expressed as a function of OCV:

$$\epsilon_{max} = \frac{\Delta_r G}{\Delta_r H} = -\frac{E_{rev} z_e \mathcal{F}}{\Delta_r H} = \frac{E_{rev}}{E_H} \quad , \text{ with } E_H = \frac{-\Delta_r H}{z_e \mathcal{F}} \quad (2.10)$$

The actual efficiency (ϵ_{cell}) of the fuel cell can be obtained from Eq. (2.10), if the actual voltage (E_{cell}) is used in place of the open-circuit voltage:

$$\epsilon_{cell} \approx \frac{E_{cell}}{E_H} \quad (2.11)$$

The equation above still bears some theoretical idealization in comparison to real operating conditions, because in practice it is found that not all the fuel feed to the cell can be utilized. For reasons to be explained in **Chapter 3**, some fuel should remain unreacted, fact that reduces the cell electric current when compared to the condition in which the fuel is fully reacted. Thus, the “real” cell efficiency is lower than that calculated by Eq. (2.11). Nonetheless, this equation serves the purpose of making it explicit that fuel cell efficiency is related to both the reversible (E_{rev}) and operating (E_{cell}) voltages. Therefore, the mathematical models that evaluate “concentration-induced losses” (or other types of losses), and their respective impact on the reduction of the cell operating voltage, are in fact trying to assess some aspect related to SOFC operating efficiency.

2.1.3 Nernst Equation

As noted before, changes in Gibbs energy can vary with temperature, pressure, concentration of chemical species, and also with electrical state properties. Particularly, the change in the Gibbs energy of reaction (2.1), for a constant temperature process, may be expressed using the activity of reactants and products^[67]

$$\Delta_r G(T, p) = \Delta_r G^\ominus(T, p) - \mathcal{R}T \ln \left(\frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (2.12)$$

where $\Delta_r G^\ominus$ is the change in Gibbs energy of reaction at a specified standard (reference $\ominus$) state; $a_i = a_i(T, p, n_{j \neq i})$ is the chemical activity of i -th species, which is a function of temperature, pressure, and the concentration of all chemical species j participating in the reaction. Equation (2.12) can be used to calculate E_{rev} , by substituting it into Eq. (2.5):

$$E_{rev} = E^\ominus + \frac{RT}{2\mathcal{F}} \ln \left(\frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (2.13)$$

where $E^\ominus$ is EMF at the reference state. Equation (2.13), which gives the EMF in terms of products/reactants, is the Nernst equation specifically for reaction (2.1). The EMF calculated from such equations is also known as the “Nernst voltage” and it is the reversible cell voltage that would exist at a given temperature, pressure, and species concentrations.

One may further manipulate Eq. (2.13) to get the explicit effects of species concentrations and system pressure. For example, if it is assumed that all the gas species behave as an ideal gas (which can be generally considered as a reasonable approximation, for the typical case of a SOFC operating at 1000 °C and 0.1 MPa), then one can write^[74]:

$$a_{H_2} = \frac{p_{H_2}}{p_\ominus} = y_{H_2} \frac{p}{p_\ominus}, \quad a_{O_2} = \frac{p_{O_2}}{p_\ominus} = y_{O_2} \frac{p}{p_\ominus}, \quad a_{H_2O} = \frac{p_{H_2O}}{p_\ominus} = y_{H_2O} \frac{p}{p_\ominus} \quad (2.14)$$

$$E_{rev} = E^\ominus + \frac{RT}{2\mathcal{F}} \ln \left[\frac{(p_{H_2}/p_\ominus) (p_{O_2}/p_\ominus)^{1/2}}{(p_{H_2O}/p_\ominus)} \right] = E^\ominus + \frac{RT}{2\mathcal{F}} \ln \left(\frac{y_{H_2} y_{O_2}^{1/2}}{y_{H_2O}} \right) + \frac{RT}{4\mathcal{F}} \ln \left(\frac{p}{p_\ominus} \right) \quad (2.15)$$

The Nernst equation (2.15) shows how the EMF of a fuel cell is related to the system pressure according to the term $RT/(4\mathcal{F}) \ln(p/p_\ominus)$. Thus, if the total pressure changes from an equilibrium state with a pressure p_1 to other with a pressure p_2 , with everything else held constant, Eq. (2.15) predicts a change of voltage

$$\Delta E_{1 \rightarrow 2} = \frac{RT}{4\mathcal{F}} \ln \left(\frac{p_2}{p_1} \right) \quad (2.16)$$

The formulae presented in the foregoing are restricted to processes obeying equilibrium thermodynamics, *i.e.* irreversible losses at electrodes are not formally taken into account. Even though the idealized behavior predicted by Eq. (2.16) is show to hold, approximately, under some operating conditions, it is not generally true, *e.g.*, raising system pressure can actually lead to a greater voltage increase than that predicted by Eq. (2.16), because it could also reduce certain irreversibilities at electrodes^[8, 75]. Moreover, Eq. (2.16) is a specific result of considering the reaction (2.1), oxidation of pure hydrogen with pure oxygen, for which the volumes of products are smaller than the cumulative volume of reactants. This may not be so in general, as in the case of the oxidation of methane, for which the cumulative volume of

reactants and products is the same (*i.e.*, there is no net change of volume; see also §3.4.2). Thus, for this reaction there is theoretically no change in the cell reversible voltage caused by the system thermodynamic pressure. This dependence on volume change ($\Delta_r \mathcal{V}$) can be easily seen by differentiating Eq. (2.6) with respect to pressure, under a constant temperature:

$$\left(\frac{\partial \Delta_r G}{\partial p}\right)_T = -z_e \mathcal{F} \left(\frac{\partial E_{rev}}{\partial p}\right)_T = \Delta_r \mathcal{V}(p) \quad \Rightarrow \quad \left(\frac{\partial E_{rev}}{\partial p}\right)_T = -\frac{\Delta_r \mathcal{V}(p)}{z_e \mathcal{F}} \quad (2.17)$$

One of the main simplifying assumptions used in this work is that cell layers (PEN) can be considered spatially isothermal. Therefore, analyses such as the temperature dependence of E_{rev} would be beyond the scope of this dissertation. Nevertheless, it is convenient to make one remark about this topic. A significant number of works by different researchers who have considered non-isothermal cases, by solving additional energy balances and heat transport equations, misprized the importance of the dependence of E_{rev} on local temperature. This is probably because there is in the literature an ingrained assumption that E_{rev} does not depend (or depends negligibly) on temperature^[4,7,8,12,67,68].

Notwithstanding such assumption is ubiquitous in the literature, it appears to be little discussion to confirm, experimentally, its generality when using it coupled to local property balances (*i.e.*, under non-equilibrium conditions). The habitual rationale^[67, 68] to “prove” that E_{rev} does not depend on temperature is to start from the Gibbs energy equation, locally assuming constant pressure and constant mole number for each and all chemical species (as in a “closed system”). Then, under these assumptions, the dependence of $E_{rev}(T)$ on temperature is disregarded for practical purposes. Nonetheless, the reference state $\mathfrak{h}$ should be selected with criterion (not too far from the cell average operating temperature). A somewhat more complete (still approximate) expression than Eq. (2.13) can be given as^[67]:

$$E_{rev} = E^{\mathfrak{h}} + \frac{\Delta_r S^{\mathfrak{h}}}{z_e \mathcal{F}} (T - T_{\mathfrak{h}}) - \frac{\mathcal{R}T}{z_e \mathcal{F}} \ln \left(\frac{\prod_i a_{product,i}^{v_i}}{\prod_j a_{reactant,j}^{v_j}} \right) \quad (2.18)$$

2.2 Fuel Cell Irreversibilities (Losses or Polarizations)

The theoretical value of the open circuit voltage (*i.e.*, at the condition of zero net current density) is given by Eq. (2.6). However, when useful current is drawn from the fuel cell, it is found that the actual voltage is often considerably less than this value^[8, 13, 68]. In the Fig. 2.1 below, a typical¹ plot of cell voltage against current density (“ $i - E_{cell}$ curve”) is shown and a number of characteristics, affecting the fuel cell performance, should be noticed:

¹ This chart is more of pedagogical value than it is typical. It might well represent a very simplistic design of a fuel cell, *e.g.* electrolyte-supported SOFC without internal fuel reforming.

Figure 2.1: Typical voltage curves: (a) low-temperature fuel cell; and (b) high-temperature fuel cell. (figure modified from [4])

- The open circuit voltage (E_{OCV}) is less than the theoretical value (E_{rev}). Although for high-temperature fuel cells (as it is case of SOFCs) the reversible "no loss" voltage is lower, the onset cell operating voltage (E_{OCV}) is usually higher, because the irreversibilities associated to this particular voltage drop ($E_{rev} - E_{OCV}$) are smaller.
- In the case of low-temperature fuel cells, there is a rapid initial fall in voltage. For SOFCs, this initial fall in voltage is less intense and sometimes almost "imperceptible" (actually, it is usually unresolved on the physical scale of interest).
- The voltage then falls less rapidly, and more linearly, as the current density increases.
- Under specific conditions, voltage falls rapidly again at higher current densities.

As already pointed out, E_{cell} can be seen as a measure of SOFC efficiency. Thus maintaining a minimum threshold for the cell voltage, even under high current loads, is critical to the successful deployment of SOFC technology. However, due to limitations of the existing technology, it is difficult to achieve high electric power density. Understanding these limitations still represents a formidable effort in the research and development of SOFCs^[13, 14, 70]. The difference between the voltage one would expect from a fuel cell operating ideally (reversibly) and the actual voltage is what entails the discussion that will follow. More specifically, that difference rooted in the “limitations of mass transport”, which is the main concern that drove this research work. The terminology used in the literature to refer to the causes of such difference (voltage drop) varies. However, herein it will be referred to as “losses”, “polarizations”, or more generally as “irreversibilities”. At times it may be also referred to as “overvoltage”, but this term when employed will refer only to those local voltage differences stemming from interfacial phenomena at the TPB of an electrode.

2.2.1 Causes of Voltage Drop

The characteristic shape of the cell i — E_{cell} curve (see figures 2.1 and 2.2) results from non-equilibrium (irreversible) processes taking place within the SOFC. There are three major losses that are usually recognized as dominant polarizations^[76, 4, 8, 68], and one minor loss that, howsoever small, will be listed here for the sake of completeness (this “minor loss” is sometimes not included in the list of electrode polarizations). These losses will be outlined just briefly in the following. “Concentration-induced losses” will be considered in more detail in **Chapter 3**; other losses will be just summarized to further the understanding of their mutual interaction, but no in-depth discussions will be presented. They are not within the scope of this work, which intends to be limited to the critical analysis of phenomena related to mass transfer.

1. Activation polarization/losses: electrode reactions involve charge (electron) transfer as a fundamental step, through which a neutral species is converted into an ion, and vice versa. The net current density is proportional to the rate of electrochemical reactions and associated with this reaction rate there is a loss in voltage, called activation polarization² or overvoltage (η_{act}). This “voltage drop” is caused by the relative slowness of reactions taking place on the surface of electrodes^[76], wherein a fraction of the “available voltage” (E_{rev}) is lost in driving the reaction that transfers electrons to or from electrodes. Charge transfer is a multi-step process, usually comprising several parallel reactions pathways, including, but not limited to: charge transfer reaction at or near the TPB; surface diffusion; surface physisorption; and competitive chemisorption. The reaction mechanism describing such multiplicity of pathways is material and microstructure-dependent, *i.e.* electrode processes and micromorphology are

² Terminology seems to be related to the thermally-activated nature of the reaction involved^[13].

closely interrelated. Thus, in practical terms, it is not feasible to propose a single, general reaction mechanism for neither cathodic (oxygen reduction) nor anodic (fuel oxidation) half-cell reactions. Moreover, it is often difficult to select a single rate-determining step (if existent, that is) and thus it is common practice in the literature to describe the overall process (“rate law”) using a phenomenological treatment (phenomenological electrode kinetics). An example of such approach is the use of phenomenological equations such as Butler-Volmer equation, Tafel equation, and the like.

2. Ohmic polarization/losses: with the exception of superconductors, matter will most certainly offer resistance to the motion of electrical charges. Ohmic polarization (η_{ohm}) is the voltage drop due to the resistance to the flow of electric charges through the materials of electrodes and the various electronic interconnections of a SOFC; it also accounts for the resistance to the flow of oxide ions through the electrolyte³. In the common case, when a linear behavior between voltage drop and current density is assumed, this polarization can be described by Ohm’s law and for this reason it is often called Ohmic loss. Such polarization is also referred to as resistive loss, a more general denotation, not restricted to Ohmic behavior. Resistive losses can be evaluated by material constitutive relations, in which specific material properties, such as the resistivity, govern the response of cell voltage to the passage of a finite current. Therefore, the transport of oxide ions through the solid electrolyte is said to be governed by its ionic resistivity; and the transport of electrons (or electron holes) through the electrodes is governed by electronic resistivities⁴. In SOFCs, the major contribution to η_{ohm} is usually from the electrolyte phase, since its ionic resistivity is fairly greater than the electronic resistivities of cathode, anode, and interconnections. Such contribution can be quite large in the case of thick electrolyte-supported cells. However, it is usually smaller in electrode-supported cells, when thin electrolytes are employed^[13].
3. Concentration polarization/losses: at (or near) the anode/electrolyte interface, electroactive fuel species (e.g., H_2 and/or CO) must be present to form the respective products (e.g., H_2O and/or CO_2) through an electrochemical oxidation reaction. Meanwhile, at (or near) the cathode/electrolyte interface, electroactive oxidant species (O_2) must be present to form the respective products (O^{2-}) through an electrochemical reduction reaction. Therefore, the transport (and *in situ* generation, when this is also the case) of fuel and oxidant within SOFC layers must be consistent with the net electric current flowing through the cell. In other words, electroactive species are adjusted through charge and mass “balance laws”, subjected to additional internal and external system constraints. The knowledge of how these species reach the electrode/electrolyte interface (*i.e.*, TPBs) informs us about what “physicochemical resistances” must be overcome, at a given current density value. These resistances are reflected as an overall

³ Or also through the electrode, when this electrode is a mixed ionic–electronic conductor (MIEC).

⁴ In a homogenized macroscale description, resistivities should be corrected for the effective medium parameters (e.g., porosity, tortuosity), and also for the possible existence of secondary contact-insulating phases.

“voltage loss” known as concentration polarization (η_{conc}). Because an “adverse concentration” is the result of the “failure to transport” sufficient electroactive species to/from the TPB region, this type of loss has been also termed as a mass transport loss (see further discussion in **Chapter 3**).

4. Electronic Leakage (parasitic losses): an ideal electrolyte should only transport ionic charges (ions) through the cell. However, this condition is often difficult to satisfy completely in practice and a certain amount of electron conduction through the electrolyte phase (“electronic leakage current”) is possible to occur^[8]. The electrical conduction in the electrolyte, though mainly carried by oxide ions, can have a small but yet deleterious contribution from electrons. This effect have a marked effect on the OCV, which is reduced by an amount η_{leak} , depending upon the electrolyte material, operating temperature, and oxygen partial pressure (p_{O_2}) profile through de cell^[8]. This voltage drop should be more acute when there is a very low oxygen partial pressure at the electrolyte/anode interface^[8]. This effect is usually not important in modern SOFC electrolyte materials and thus it is often disregarded in most modeling studies (as will be seen in **Chapter 4**).

Figure 2.2: schematic-only $i-E_{cell}$ curve. The voltage is a decreasing function of current density due to unavoidable losses (polarizations). The more electric current that is drawn from the cell, the greater these losses are. Each of these losses can be associated with some underlying non-equilibrium process. Polarization regions may (and often do) overlap, and thus they cannot be separated in a strict sense, as in this figure^[68].

2.2.2 Distinguishing and Combining Different Irreversibilities

From a mathematical modeling perspective, it is convenient to formulate an equation that would bring together all the previously mentioned irreversibilities (η_{act} , η_{ohm} , η_{conc} , η_{leak}) and relate them with the actual cell voltage (E_{cell}). This equation could be used, for instance, for either calculating the cell voltage or to distinguish between losses. However, such equation requires, for its formulation, some degree of arbitrariness on how to define each of the irreversibilities separately, because polarization regions may (and often do) overlap, and thus they cannot be separated in a strict sense.

Two main assumptions are made to support the formulation of this equation: (i) that a continuum description can be applied on the electrode-level; and (ii) the presumed additivity of “voltage losses”. Although the additivity property assumption could be proved for systems under thermodynamic equilibrium, this is not so for those under non-equilibrium conditions^[77, 78]. The last statement is surely ambiguous, as these voltage losses can only exist under non-equilibrium conditions. The usual workaround in the literature, to deal with this “teleological hindrance”, is to invoke the local equilibrium postulate^[79, 80]. In this work, this assumption is taken as a valid precept. Nevertheless, the point here is to emphasize that, although empirically correct, the yet-to-be-proposed equation should be considered already in a simplified form to the detriment of its usefulness and practicality.

At zero net current, SOFC electrodes should provide (theoretically) the thermodynamic or reversible voltage ($E_{cell} = E_{rev}$). The connection of a load, thereby closing the electrical circuit, should induce a net current density (i) in the SOFC and reduce E_{cell} by the overall value of voltage losses, $E_{loss} = E_{loss}(i)$. Thus the current drawn from the cell “costs” some potential and the thermodynamically predicted voltage (E_{rev}) may be viewed as the “capital” at one’s disposal^[12].

$$E_{cell}(i) = E_{rev} - E_{loss}(i) \quad (2.19)$$

Equation (2.19) is assumed to be valid at steady-state condition, at a given space coordinate. Moreover, in Eq. (2.19) the Nernst voltage E_{rev} is assumed not to be a function of i . This assumption is valid if, for instance, the mass transport rates of fuel and oxidant are sufficiently high so that species concentrations in gas channels (or at other adequate reference condition) are invariant with respect to current density. Otherwise, E_{rev} must be treated as a function of i :

$$E_{cell}(i) = E_{rev}(i) - E_{loss}(i) \quad (2.20)$$

Thus, the difference $E_{rev}(i) - E_{rev}(i + \delta i)$ may be understood as a measure of the change in the reference composition of gas-phase (at constant T and p), due to a finite change δi in the

current. As it will be explained further below, the correct definition of E_{rev} and E_{loss} depends on where one chooses the “reference gas concentration” to be located at. For instance, either at the bulk of gas channels (E_{rev}^{bulk}) or at the percolated TPB regions (E_{rev}^{TPB}). Equation (2.20) suggests that one may calculate the actual cell voltage output, starting with the thermodynamic predicted voltage and then subtracting out all the losses (voltage drops):

$$E_{cell} = E_{rev} - \eta_{ohm} - \eta_{act} - \eta_{conc} - \eta_{leak} \quad (2.21)$$

Equation (2.21) sets a convenient way to depict the combined effects from the major phenomena that affect SOFC power throughput. For this reason, this equation has been used in the literature as a baseline for a wide spectrum of modeling techniques: from microscopic to macroscopic scale models; from phenomenological differential forms, to algebraic experimentally-fitted engineering forms (e.g., empirical distributed-parameter models). Therefore, both the general form of Eq. (2.21) and specific expressions (submodels) for the different irreversibilities vary widely, depending on the modeling approach^[1, 2, 72, 81]. Deceptively simple in appearance, this equation can “encapsulate” quite sophisticated models to calculate each type of polarization, thus supporting complex numerical simulations of SOFCs (see **Chapter 4**). Some additional remarks about Eq. (2.21):

- This equation, even when applied with seemingly basic fuel cell submodels, has been found to give good fit with the results of real SOFCs, based on evidence derived from experiments^[4, 8].
- The question of which processes contribute to E_{loss} , how large is each contribution, and in what conditions they contribute, dictates the final format of this equation. Thus, to simplify this equation, one usually neglects the terms with little impact on operating losses. For important terms, the desired accuracy is crucial criterion for selecting the modeling complexity of each submodel in Eq. (2.21).
- As a phenomenological equation derived based on energy conservation, its theoretical background (e.g., supporting assumptions) is evaluated by its verifiable empirical consequences, independently of any fundamental model possibly supporting it. This implies more freedom in the interpretation and use of formulas based on Eq. (2.21).

Equation (2.21) can also be casted into a form that makes the problem’s dimensionality explicit, for example, when solving the one-dimensional distribution of cell voltage along the bulk flow direction (x) of the SOFC. This form not only allows to pinpoint the highest achievable EMF (E_{rev}) in the cell, but also the influence of the local current density $i(x)$. For instance, this local description can help to identify regions where highly concentrated current densities are present and then verify whether a failure mechanism might be associated with

high localized values^[8]. When used for calculating local electrochemical quantities, this equation may be rewritten as:

$$E_{cell} = E_{rev}(x) - \eta_{ohm}(x) - \eta_{act}(x) - \eta_{conc}(x) - \eta_{leak}(x) \quad (2.22)$$

Where the cell voltage E_{cell} is held invariant along the fuel flow direction. This is the case when the SOFC operation is assumed iso-potential along the x direction (*i.e.*, when the electrical resistance of current-collecting bus bars along the flow direction is much lower than that of PEN's through-plane direction). This assumption is mostly true in real, “well designed” SOFCs^[7, 8, 29]. Thus, at first, it can be adopted for the purposes of this work. The concentration and activation polarizations can be further divided into anodic and cathodic contributions,

$$\eta_{act} = \eta_{A,an} + \eta_{A,ca} \quad (2.23)$$

$$\eta_{conc} = \eta_{C,an} + \eta_{C,ca} \quad (2.24)$$

$$\eta_{an} = \eta_{A,an} + \eta_{C,an} \quad (2.25)$$

$$\eta_{ca} = \eta_{A,ca} + \eta_{C,ca} \quad (2.26)$$

Thus to give⁵,

$$E_{cell} = E_{rev} - \eta_{ohm} - \eta_{leak} - \eta_{A,an} - |\eta_{A,ca}| - \eta_{C,an} - |\eta_{C,ca}| \quad (2.27)$$

Figure 2.3 illustrates the basic idea conveyed by Eq. (2.27): part of the thermodynamic available voltage must be “sacrificed” to produce a net current (for simplicity, only activation and ohmic polarizations have been indicated on this figure). More specifically, cell operation requires sacrificing a fraction of both anode and cathode Galvani potentials⁶, which are lowered by $\eta_{A,an}$ and $\eta_{A,ca}$, respectively^[68]. Within the electrolyte, voltage gradient is present in order to drive the transport of charges down the cell and, as charge transport is not a “frictionless process”, it results in a voltage loss of η_{ohm} . Here it is important to add some elucidative comments concerning the voltage profiles as shown on Fig. 2.3:

- Electrolyte was assumed as a purely ionic-conducting material and the electrodes as ideal electronic conductors. Thus no ohmic losses were considered in the electrodes.
- Electrode activation polarizations are not physically meaningful differences in terms of electric/electrostatic potentials. That is, they do not represent real potential drops along a given electric potential profile (*e.g.*, blue line), but a

⁵ Explanations for the use of absolute values in the case of cathodic terms will be provided in the next pages.

⁶ Galvani potentials are said to be “equilibrium interfacial potentials”, at anode/electrolyte and cathode/electrolyte reaction interfaces, which must sum to give the overall reversible voltage (see also §§2.3.1 and §§2.3.2).

“virtual” potential difference between polarised and unpolarised cases (the difference between the red and blue lines).

- In this specific example, the measured cell voltage was given as the sum of electric potentials differences at the anode and cathode sides. Thus, from Fig. 2.3 one has:

$$E_{cell} = (\Delta\phi_{eq,an} - \eta_{A,an}) + (\Delta\phi_{eq,ca} - \eta_{A,ca}) = E_{rev} - \eta_{A,an} - \eta_{A,ca} \quad (2.28)$$

Figure 2.3: hypothetical voltage profiles in a SOFC, with red line indicating the condition of thermodynamic equilibrium. (a) Effect of anode and cathode activation losses. (b) Effect of ohmic losses. Here, Galvani potentials are evaluated with reference to the electrolyte potential (figure by the author based on an example from [68]).

In the specific case of Eq. (2.28) (and thus of Fig. 2.3), both Eq. (2.26) and Eq. (2.27) hold. As will be discussed further below, a stricter definition of activation polarizations will reveal that $\eta_{A,ca}$ is indeed the absolute value of the cathodic overvoltage, that is $|\eta_{A,ca}|$:

$$\Delta\phi - \Delta\phi_{eq} \equiv \eta_{act} \quad (2.29)$$

Where $\Delta\phi_{eq}$ is the equilibrium electrode potential step (in relation to some defined reference) and $\Delta\phi$ is the actual (or imposed) electrode potential step. The “stricter” definition of Eq. (2.29)

has been applied in several works from the literature, as in Fig. 2.4^[72], in which the voltage profile $\Delta\phi = \Delta\phi(z)$ is explicitly solved for through the PEN thickness. Nonetheless, it should be mentioned that the definition given by Eq. (2.29) is not the only one found in the literature, in terms of sign (*i.e.*, polarity) convention.

Figure 2.4: Simulated distributions of the electric potential in a polarized SOFC (figure modified from [72]).

In the example of Fig. 2.4, electric potentials were reflected around the abscissa axis in comparison with Fig. 2.3, and the cathode side is now grounded (set to zero) as a fixed reference. In Fig. 2.4, the cell voltage is given by

$$E_{cell} = \phi_{ca} - \phi_{an} \quad (2.30)$$

where ϕ_{ca} and ϕ_{an} are the electric potentials of the cathode and anode, respectively (ϕ_{ca} was set to zero as reference). Electrodes are at different potentials as a result of the two electric potential steps that form at electrical double-layers^[67], at the anode/electrolyte and cathode/electrolyte interfaces, $\Delta\phi_{an}$ and $\Delta\phi_{ca}$, respectively:

$$\begin{aligned} \Delta\phi_{ca} &= \phi_{ca} - \phi_{elyt,ca} > 0 \\ \Delta\phi_{an} &= \phi_{an} - \phi_{elyt,an} < 0 \end{aligned} \quad (2.31)$$

where $\phi_{elyt,ca}$ and $\phi_{elyt,an}$ are the electric potentials in the electrolyte just beyond the space-charge-region, on the cathode and anode sides, respectively. Thus, from Eq. (2.30) and (2.31)

$$E_{cell} = \Delta\phi_{ca} - \Delta\phi_{an} + (\phi_{elyt,ca} - \phi_{elyt,an}) = \Delta\phi_{ca} - \Delta\phi_{an} + \Delta\phi_{ohm} \quad (2.32)$$

Now comparing Eq. (2.32) with (2.28), taking into consideration Eq. (2.31) and (2.29), and also knowing in this case^[67] that $\Delta\phi_{ca} < \Delta\phi_{ca,eq}$ and $\Delta\phi_{an} > \Delta\phi_{an,eq}$, one finds that:

$$\begin{aligned} \Delta\phi_{ca} &= (\eta_{A,ca}^* + \Delta\phi_{ca,eq}) \Leftrightarrow \eta_{A,ca}^* < 0 \Rightarrow \eta_{A,ca}^* = -\eta_{A,ca} \\ \Delta\phi_{an} &= (\eta_{A,an}^* + \Delta\phi_{an,eq}) \Leftrightarrow \eta_{A,an}^* > 0 \Rightarrow \eta_{A,an}^* = \eta_{A,an} \end{aligned} \quad (2.33)$$

$$\Delta\phi_{ohm} = -(\phi_{elyt,an} - \phi_{elyt,ca}) = -\eta_{ohm}$$

Note the signal change in front of $\eta_{A,ca}$. These formulations are indeed awkward when describing “antiparallel processes” occurring at the anode and cathode, where the faradaic net current changes signal, and such formulations are at times source of errors in the literature. For instance, a number of authors admit the absolute value of cathodic activation polarization in Eq. (2.27), not considering the same treatment for the cathodic concentration polarization. This could suggest the interpretation that

$$E_{cell} = E_{rev} - \eta_{A,an} - \eta_{C,an} - |\eta_{A,ca}| - \eta_{C,ca} - \eta_{ohm} \quad (2.34)$$

which is incorrect, because in the case of Fig. 2.4, which is based on the definitions of Eq. (2.30) and (2.31), both $\eta_{A,ca}$ and $\eta_{C,ca}$ are negative signed (cathodic polarity). Thus, in Eq. (2.34) $\eta_{C,ca}$ is added to E_{rev} instead of being subtracted from it. One could alter the definition of the concentration polarization $\eta_{C,ca}$ so it results positive, but such procedure lacks thermodynamic consistency (see discussion in §§3.3). There are other situations in which $\eta_{A,an}$ and $\eta_{A,ca}$ might lead to issues with regard to their signals. For example, when using Tafel approximation in the low current limit^[67]. The important remark is that Eq. (2.27) is a statement of the first law of thermodynamics and, as such, should be intrinsically consistent. The mere use of absolute values appears to be an artifice (see discussion in §§2.3.1 and §§2.3.2). Nonetheless, the fact that $\eta_{A,an}$ is positive and $\eta_{A,ca}$ is negative depicts a real physical situation where electrochemical reactions proceed in the anodic direction at the anode and in the cathodic direction at the cathode (assuming that the definition given by Eq. (2.29) is equally applied to both cathode and anode).

In Eq. (2.27) the concentration polarization can be accounted for in different ways, for which there are two frequently used approaches. The first one proposes a submodel to calculate η_{conc} (thus $\eta_{C,an}$ and $\eta_{C,ca}$) and is commonly referred to as one having an explicit (often semi-empirical) evaluation of concentration polarization^[82]. The other approach does not prescribe a particular expression to η_{conc} . In fact, in this approach, this term does not (explicitly) appear. The latter modeling technique^[83, 72, 84, 85] considers additional mass transfer governing equations to solve for the concentration of electrochemical species at the TPBs. In this case, Eq. (2.27) is slightly modified:

$$E_{cell} = E_{rev}^{TPB} - \eta_{ohm} - \eta_{leak} - \eta_{A,an} - |\eta_{A,ca}| \quad (2.35)$$

Where E_{rev}^{TPB} is the Nernst voltage evaluated at the TPB. For example, in the case of reaction (1.2),

$$E_{rev}^{TPB} = E^\circ + \frac{RT}{2\mathcal{F}} \ln \left[\frac{(p_{H_2,tpb}/p^\circ)_{an} (p_{O_2,tpb}/p^\circ)^{1/2}}{(p_{H_2O,tpb}/p^\circ)_{an}} \right] \quad (2.36)$$

where $p_{H_2,tpb}$ and $p_{H_2O,tpb}$ are the partial pressures of H_2 and H_2O at anodic TPBs; $p_{O_2,tpb}$ is the partial pressure of O_2 at cathodic TPBs. Therefore, this latter approach implicitly evaluates η_{conc} inside the term E_{rev}^{TPB} (i.e., it evaluates the result of $E_{rev}^{bulk} - \eta_{C,an} - |\eta_{C,ca}|$). Still using the example of reaction (1.2), Eq. (2.35) can be obtained using the following definitions (see §§3.3.1 for the respective derivation):

$$\eta_{C,an} = \frac{RT}{2\mathcal{F}} \ln \left(\frac{p_{H_2,bulk}}{p_{H_2,tpb}} \frac{p_{H_2O,tpb}}{p_{H_2O,bulk}} \right) \geq 0 \quad (2.37)$$

$$\eta_{C,ca} = \frac{RT}{4\mathcal{F}} \ln \left(\frac{p_{O_2,tpb}}{p_{O_2,bulk}} \right) \leq 0 \quad \Rightarrow \quad |\eta_{C,ca}| = \frac{RT}{4\mathcal{F}} \ln \left(\frac{p_{O_2,bulk}}{p_{O_2,tpb}} \right) \quad (2.38)$$

Note that Eq. (2.37) and (2.38) are just possible definitions for the anode and cathode concentration polarizations (see **Chapter 3**) and not actual modeling equations. Substituting Eq. (2.37) and (2.38) in Eq. (2.27), and also making use of Eq. (2.15), yields:

$$\begin{aligned} E_{cell} &= -\eta_{ohm} - \eta_{leak} - \eta_{A,an} - |\eta_{A,ca}| + E^\circ + \\ &+ \frac{RT}{2\mathcal{F}} \left\{ \ln \left[\frac{(p_{H_2,bulk}/p^\circ) (p_{O_2,bulk}/p^\circ)^{1/2}}{(p_{H_2O,bulk}/p^\circ)} \right] - \ln \left(\frac{p_{H_2,bulk}}{p_{H_2,tpb}} \frac{p_{H_2O,tpb}}{p_{H_2O,bulk}} \right) - \ln \left(\frac{\sqrt{p_{O_2,bulk}}}{\sqrt{p_{O_2,tpb}}} \right) \right\} \\ \Rightarrow E_{cell} &= -\eta_{ohm} - \eta_{leak} - \eta_{A,an} - |\eta_{A,ca}| + E^\circ + \\ &+ \frac{RT}{2\mathcal{F}} \ln \left[\frac{(p_{H_2,tpb}/p^\circ) (p_{O_2,tpb}/p^\circ)^{1/2}}{(p_{H_2O,tpb}/p^\circ)} \right] \\ \therefore E_{cell} &= -\eta_{ohm} - \eta_{leak} - \eta_{A,an} - |\eta_{A,ca}| + E_{rev}^{TPB} \end{aligned} \quad (2.39)$$

2.3 Theoretical Considerations and Inconsistencies in Defining SOFC Polarizations

2.3.1 Clarifications on Polarizations and Potential Steps

There are several, though not arbitrary, ways to elaborate the necessary set of equations concerning the definition of electric (inner) potentials and their differences, electromotive “forces”, and polarizations. Nevertheless, thermodynamic consistency should be ensured and results must be physically meaningful (e.g., negative charges in order to perform work should not flow from high potential states to lower potential states). Firstly, one needs to establish certain primary definitions to close the set of equations, or otherwise one will end up

running around in a circle. The starting point is the definition of activation polarization and, most importantly, its sign (polarity) convention.

$$\Delta\phi_{an} - \Delta\phi_{eq,an} \equiv \eta_{A,an} \quad (2.40)$$

$$\Delta\phi_{ca} - \Delta\phi_{eq,ca} \equiv \eta_{A,ca} \quad (2.41)$$

Equations (2.40) and (2.41) indicate that shifting the electrode-electrolyte potential step ($\Delta\phi$) in relation to the equilibrium value ($\Delta\phi_{eq}$) will bias the direction of the electrochemical reaction (see Fig. 2.5). If the electrode/electrolyte potential step is made relatively more negative than the equilibrium Galvani potential, that is $\eta_{act} < 0$, the reaction will be biased towards the reduction process. On the other hand, if the potential step is made relatively more positive than the equilibrium value, $\eta_{act} > 0$, the reaction will be biased toward the oxidation process. Accordingly, if $\eta_{act} = 0$ the potential step equals that of thermodynamic equilibrium and oxidation and reduction half-processes are balanced at a given TPB^[68] (see also §2.3.2).

Figure 2.5: By changing the electrode potential one can trigger reduction (left) or oxidation (right) processes. The situation in the middle corresponds to the thermodynamic equilibrium (figure adapted from [68]).

Once η_{act} has been defined by Eq. (2.40) and (2.41), the reasoning on how to express $\Delta\phi$ is an important aspect that some works in the literature^[72] overlook. This aspect can cause confusion when deriving the Nernst equation for half-cell reactions. In principle, the potential step might be evaluated as either $\Delta\phi = \phi_{elde} - \phi_{elyt}$ or $\Delta\phi = \phi_{elyt} - \phi_{elde}$. Before specifying which of the two definitions to use, a few more mathematical assertions should be elaborated. Let the electrochemical potential $\tilde{\mu}_i$ for the i -th species be expressed by^[67]

$$\tilde{\mu}_i = \mu_i + z_e \mathcal{F} \phi_i = \mu_i^\ominus + \mathcal{R}T \ln a_i + z_i \mathcal{F} \phi_i \quad (2.42)$$

Assuming that the respective electrochemical potentials are offsetting one another to maintain the thermodynamic equilibrium, one can write, for a generic electrochemical reaction, that

$$\left(\sum_i \nu_i \mu_i \right)_{\text{products}} - \left(\sum_j \nu_j \mu_j \right)_{\text{reactants}} = -\Delta z_e \mathcal{F} \Delta \phi_i \quad (2.43)$$

Here $\Delta \phi_i$ represents the “built-up electrical potential” for charges that “are moved” on the reaction sites, per-mole basis of a given reactant (see also §§3.2 and §§3.3.1 for further clarifications). Now, specifically for the anode of a SOFC, consider the following electrochemical reaction formulated in a Kröger–Vink notation^[18]:

Applying Eq. (2.42) and Eq. (2.43) for reaction (2.44), then⁷

$$\begin{aligned} \mu_{H_2O}^{\ddagger} + \mathcal{R}T \ln a_{H_2O,tpb} + \mu_{V_O^{\bullet\bullet}}^{\ddagger} + 2\mu_{e'}^{\ddagger} - 2\mathcal{F} \phi_{e'}^{tpb} - \left[\mu_{H_2}^{\ddagger} + \mu_{O_O^{\times}}^{\ddagger} + \mathcal{R}T \ln a_{H_2,tpb} + \right. \\ \left. + \mathcal{R}T \ln a_{O_O^{\times},tpb} - 2\mathcal{F} \phi_{O_O^{\times}}^{tpb} \right] = 0 \\ \Rightarrow 2\mathcal{F} \left(\phi_{O_O^{\times}}^{tpb} - \phi_{e'}^{tpb} \right) = - \left(\mu_{H_2O}^{\ddagger} + \mu_{V_O^{\bullet\bullet}}^{\ddagger} + 2\mu_{e'}^{\ddagger} - \mu_{H_2}^{\ddagger} - \mu_{O_O^{\times}}^{\ddagger} \right) - \mathcal{R}T \ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} a_{O_O^{\times},tpb}} \right) \\ \Rightarrow \phi_{O_O^{\times}}^{tpb} - \phi_{e'}^{tpb} = -\frac{\Delta G_{an}^{\ddagger}}{2\mathcal{F}} - \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} a_{O_O^{\times},tpb}} \right) \end{aligned} \quad (2.45)$$

For the cathode of an SOFC the result is analogous, but considers the following overall reaction^[8]:

Thus,

$$\begin{aligned} \mu_{O_O^{\times}}^{\ddagger} + \mathcal{R}T a_{O_O^{\times},tpb} - 2\mathcal{F} \phi_{O_O^{\times}}^{tpb} - \left(\frac{1}{2} \mu_{O_2}^{\ddagger} + \frac{1}{2} \mathcal{R}T \ln a_{O_2,tpb} + \mu_{V_O^{\bullet\bullet}}^{\ddagger} + 2\mu_{e'}^{\ddagger} - 2\mathcal{F} \phi_{e'}^{tpb} \right) = 0 \\ \Rightarrow 2\mathcal{F} \left(\phi_{e'}^{tpb} - \phi_{O_O^{\times}}^{tpb} \right) = - \left(\mu_{O_O^{\times}}^{\ddagger} - \mu_{V_O^{\bullet\bullet}}^{\ddagger} - 2\mu_{e'}^{\ddagger} - \frac{1}{2} \mu_{O_2}^{\ddagger} \right) - \mathcal{R}T \ln \left(\frac{a_{O_O^{\times},tpb}}{\sqrt{a_{O_2,tpb}}} \right) \\ \Rightarrow \phi_{e'}^{tpb} - \phi_{O_O^{\times}}^{tpb} = -\frac{\Delta G_{ca}^{\ddagger}}{2\mathcal{F}} - \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{O_O^{\times},tpb}}{\sqrt{a_{O_2,tpb}}} \right) \end{aligned} \quad (2.47)$$

And from Eq. (2.45) and (2.47),

$$\begin{aligned} 2\mathcal{F} \left(\phi_{e'}^{tpb} - \phi_{O_O^{\times},ca}^{tpb} + \phi_{O_O^{\times},an}^{tpb} - \phi_{e'}^{tpb} \right) = -(\Delta G_{an}^{\ddagger} + \Delta G_{ca}^{\ddagger}) - \mathcal{R}T \ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} \sqrt{a_{O_2,tpb}}} \right) \\ \Rightarrow \left(\phi_{e'}^{tpb} - \phi_{O_O^{\times},ca}^{tpb} \right) + \left(\phi_{O_O^{\times},an}^{tpb} - \phi_{e'}^{tpb} \right) = -\frac{\Delta G^{\ddagger}}{2\mathcal{F}} - \frac{\mathcal{R}T}{2\mathcal{F}} \left[\ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} \sqrt{a_{O_2,tpb}}} \right) + \ln \left(\frac{a_{O_O^{\times},tpb,ca}}{a_{O_O^{\times},tpb,an}} \right) \right] \end{aligned} \quad (2.48)$$

⁷ The activity of $V_O^{\bullet\bullet}$ does (usually) not appear in Eq. (2.45) since $a_{O_O^{\times}}$ is considered to be the activity of the building element ($O_O^{\times} - V_O^{\bullet\bullet}$) and also contains configurational effects with respect to $V_O^{\bullet\bullet}$ (see [108] for details). At this point, $O_O^{\times}$ represents incorporated oxygen in the form of O^{2-} in the bulk phase (i.e., an interstitial defect).

Note that for the anode, Eq. (2.45), the LHS is given by $\phi_{O_2^{\times}}^{tpb} - \phi_e^{tpb}$, whereas for the cathode, Eq. (2.47), the LHS is $\phi_e^{tpb} - \phi_{O_2^{\times}}^{tpb}$; that is, electric potentials are reversed in order. The sum of both anodic and cathodic equations gives the Nernst equation for the cell, Eq. (2.48), which express the electromotive “force” (E_{rev}) of the SOFC (for comparison, see Eq. (2.6) and (2.13)):

$$E_{rev} = \left(\phi_e^{tpb} - \phi_{O_2^{\times}}^{tpb} \right)_{ca} + \left(\phi_{O_2^{\times}}^{tpb} - \phi_e^{tpb} \right)_{an} \quad (2.49)$$

At this point one might wonder about the respective definitions of $\Delta\phi_{eq,ca}$ and $\Delta\phi_{eq,an}$, when taking into consideration the result of Eq. (2.49): whether it is possible to assert that

$$\Delta\phi_{eq,ca} = \left(\phi_e^{tpb} - \phi_{O_2^{\times}}^{tpb} \right)_{ca}, \Delta\phi_{eq,an} = \left(\phi_{O_2^{\times}}^{tpb} - \phi_e^{tpb} \right)_{an}, \text{ and thus } E_{rev} = \Delta\phi_{eq,ca} + \Delta\phi_{eq,an}.$$

Or, alternatively,

$$\Delta\phi_{eq,an} = - \left(\phi_{O_2^{\times}}^{tpb} - \phi_e^{tpb} \right)_{an}, \text{ and thus } E_{rev} = \Delta\phi_{eq,ca} - \Delta\phi_{eq,an}.$$

It stands to reason that this question refer to the same problem on how to define $\Delta\phi$. The absolute electrode-electrolyte (or Galvani) potential difference ($\Delta\phi$) is a conceptual synthesis of two individual sources of potential difference through electrified interfaces (*i.e.*, electric double-layers): it is, theoretically, the sum of potential differences due to charge separation and dipole orientation^[86], as will be seen from the discussion to follow. The Galvani potential difference across the phase boundary (interface) of a metal(*M*)-electrolyte(*S*) can be identified as the difference of two inner potentials, ϕ_M and ϕ_S :

$$\Delta\phi_{M,S} = \phi_M - \phi_S \quad (2.50)$$

where $\Delta\phi_{M,S}$ represents the difference of inner potentials of the bulk phases *M* and *S*. The potential through an electrochemical system, which is a succession of interfaces, is the sum of all the potential differences through these interfaces. Since each interfacial potential difference is a difference of inner potentials, the potential difference through the cell may be written as the sum of all the inner potentials at the various interfaces^[86]:

$$E_{cell} = \Delta\phi_{M_1,S} + \sum_j (\Delta\phi_{PB})_j \quad (2.51)$$

Where $\Delta\phi_{M_1,S}$ represents the difference of inner potentials of the phases M_1 and *S*, and $(\Delta\phi_{PB})_j$ is the $\Delta\phi$ across the *j*-th extra phase boundary. Consider a simple system (or cell) made up of the interfaces M_1/S , S/M_2 , and M_2/M_1'' , with M_1'' being the same metal as M_1 . If the potential difference through this system is written in an expanded form using Eq. (2.51), then

$$\begin{aligned}
E_{cell} = (\Delta\phi)_{cell} &= \Delta\phi_{M_1,S} + \Delta\phi_{S,M_2} + \Delta\phi_{M_2,M_1''} \\
&= (\phi_{M_1} - \phi_S) + (\phi_S - \phi_{M_2}) + (\phi_{M_2} - \phi_{M_1''}) \\
&= (\phi_{M_1} - \phi_{M_1''})
\end{aligned} \tag{2.52}$$

Therefore, from Eq. (2.49) and (2.52) one can argue that, under thermodynamic equilibrium (*i.e.*, zero net current density),

$$E_{rev} = \phi_{e^-,an}^{tpb} - \phi_{e^-,ca}^{tpb} = \phi_{ca}(i=0) - \phi_{an}(i=0) \tag{2.53}$$

And accordingly,

$$E_{cell}(i) = \phi_{ca}(i) - \phi_{an}(i) \tag{2.54}$$

Which is the same as Eq. (2.30). Finally, one should note that both the definition of $\Delta\phi$ and the particular form of Eq. (2.40) and (2.41) are interrelated. To illustrate this point, let us admit the following definition for $\Delta\phi$ as suggested by Eq. (2.52):

$$\begin{aligned}
\Delta\phi_{ca} &= \phi_{ca} - \phi_{elyt,ca} \\
\Delta\phi_{an} &= \phi_{elyt,an} - \phi_{an}
\end{aligned} \tag{2.55}$$

$$E_{cell} = \phi_{ca} - \phi_{an} = (\Delta\phi_{ca} + \phi_{elyt,ca}) + (\Delta\phi_{an} - \phi_{elyt,an}) = \Delta\phi_{ca} + \Delta\phi_{an} - \eta_{ohm} \tag{2.56}$$

Substituting Eq. (2.40) and (2.41) in Eq. (2.56), then

$$\begin{aligned}
E_{cell} &= (\Delta\phi_{eq,ca} + \Delta\phi_{eq,an}) + \eta_{act,ca} + \eta_{act,an} - \eta_{ohm} \\
E_{cell} &= E_{rev} + \eta_{act,ca} + \eta_{act,an} - \eta_{ohm}
\end{aligned} \tag{2.57}$$

where $E_{rev} = \Delta\phi_{eq,ca} + \Delta\phi_{eq,an}$. In Eq. (2.57), however, the value of $\eta_{act,an}$ is added to E_{rev} unless

$$\eta_{act,an} = \Delta\phi_{an} - \Delta\phi_{eq,an} < 0 \Leftrightarrow \Delta\phi_{an} < \Delta\phi_{eq,an} \tag{2.58}$$

which is the opposite situation depicted for the anode case, in that the reaction should be biased toward the oxidation (anodic) process, when the electrode-electrolyte potential step is made relatively more positive than the equilibrium potential. As a result of this incongruence, one concludes that Eq. (2.31) must be used with Eq. (2.40) and (2.41), in lieu of Eq. (2.55):

$$\begin{aligned}
\Delta\phi_{ca} &= \phi_{ca} - \phi_{elyt,ca} \\
\Delta\phi_{an} &= \phi_{an} - \phi_{elyt,an}
\end{aligned}$$

In other words, Eq. (2.40) and Eq. (2.41), when combined with the sign convention established for η_{act} (see Fig. 2.5), results in the definition of $\Delta\phi$ as expressed by Eq. (2.30). Moreover, this latter equation is consistent with the formal macroscopic definition/interpretation of $\Delta\phi$ (see §§2.3.2).

As mentioned earlier, the potential difference $\Delta\phi$ through an electrified electrode-electrolyte Interface is the sum of two different potential differences^[86]: one due to charge separation (ψ) and the other due to dipole orientation (χ). Each of these potential differences represent the work needed to transport a unit test charge from infinity in vacuum, through dipole layers, to a point located at a charged electrolyte or electrode (see Fig. 2.6). One should differentiate between the concepts of electric potential and Galvani (inner) potential. The former is a more comprehensive physical quantity, which also includes Galvani potentials (both are scalar quantities measured in Volts and that can be associated with some electrical energy scale). The latter, however, besides being quantified as an electric potential, has a specific meaning: ϕ represents the electrical work needed when a charged particle is transferred from infinite separation in vacuum through a surface shell, which contains excess charges and oriented dipoles.

Figure 2.6: schematics for the definition of ϕ at a point P . ϕ is related to the total work done in bringing a unit test charge (over each acts columbic forces F_z) along the z axis, from infinity up to that point P , just inside a given bulk phase (electrolyte or electrode). (figure by the author).

Therefore, the definition of Galvani potential requires the presence of charged interfaces, whereas electric potentials, in general, do not. The Galvani potential difference ($\Delta\phi$) has an even more specific meaning: it is a surface potential difference between two potentials through the

phase boundary of dissimilar materials, and which is evaluated in a very definite way (see Fig. 2.6 to recognize in what reference direction the potential differences are considered):

$$\Delta\phi_{elde/elyt} = \Delta\phi_{elyt/elde} = \Delta\phi_{elde} = \phi_{elde} - \phi_{elyt} \quad (2.59)$$

where $\Delta\phi_{elde}$ is calculated as the inner potential of electrode minus the inner potential of electrolyte, just beyond the space charge zone, regardless of the direction of electric current. Note that Eq. (2.59) matches exactly the definition of Eq. (2.31). In section §§2.3.2, $\Delta\phi$ is addressed from the perspective of Eq. (2.40) and (2.41), *i.e.*, from the perspective of the “driving force” for the charge-transfer reaction. Therein the sign of $\Delta\phi$ is shown to be, again, physically relevant.

So to conclude this section, a set of consistent equations is summarized below based on the definitions of Eq. (2.40) and (2.41), and on the sign convention of Fig. 2.5. In the derivation of these equations it was assumed that, for time-invariant systems, the following definition of a “generic electromotive force” (E) holds:

$$E_{[A,B]} = - \int_A^B \nabla\phi \cdot d\vec{l} = \phi_A - \phi_B = -(\phi_B - \phi_A) \quad (2.60)$$

$$E_{[B,C]} = E_C - E_B = E_{[ref,C]} - E_{[ref,B]} = -(\phi_C - \phi_{ref}) + (\phi_B - \phi_{ref}) = -(\phi_C - \phi_B) \quad (2.61)$$

Where ϕ_{ref} may represent an equilibrium, nonpolarisable reference electrode.

$$\Delta\phi_{eq,an}^{tpb} = \phi_{e^-,an}^{tpb} - \phi_{O_o^{\times},an}^{tpb} \quad (2.62)$$

$$\Delta\phi_{eq,ca}^{tpb} = \phi_{e^-,ca}^{tpb} - \phi_{O_o^{\times},ca}^{tpb} \quad (2.63)$$

$$-\Delta\phi_{eq,an}^{tpb} = -\frac{\Delta G_{an}^{\ddagger}}{2\mathcal{F}} - \mathcal{RT} \ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} a_{O_o^{\times},tpb}} \right) \quad (2.64)$$

$$+\Delta\phi_{eq,ca}^{tpb} = -\frac{\Delta G_{ca}^{\ddagger}}{2\mathcal{F}} - \mathcal{RT} \ln \left(\frac{a_{O_o^{\times},tpb}}{\sqrt{a_{O_2,tpb}}} \right) \quad (2.65)$$

$$\Delta\phi_{eq,ca}^{tpb} - \Delta\phi_{eq,an}^{tpb} = -\frac{\Delta G^{\ddagger}}{2\mathcal{F}} - \frac{\mathcal{RT}}{2\mathcal{F}} \left[\ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} \sqrt{a_{O_2,tpb}}} \right) + \ln \left(\frac{a_{O_o^{\times},tpb,ca}}{a_{O_o^{\times},tpb,an}} \right) \right] \quad (2.66)$$

$$E_{cell} = \phi_{ca} - \phi_{an} \quad (2.67)$$

$$\Delta\phi_{ca} = \phi_{ca} - \phi_{elyt,ca} \quad (2.68)$$

$$\Delta\phi_{an} = \phi_{an} - \phi_{elyt,an}$$

$$E_{cell} = \Delta\phi_{ca} - \Delta\phi_{an} + \Delta\phi_{ohm} \quad (2.69)$$

$$\Delta\phi_{ohm} = \phi_{elyt,ca} - \phi_{elyt,an} = -\eta_{ohm} \quad (2.70)$$

$$E_{cell} = \Delta\phi_{eq,ca} - \Delta\phi_{eq,an} + \eta_{A,ca} - \eta_{A,an} - \eta_{ohm} \quad (2.71)$$

$$E_{rev} = \Delta\phi_{eq,ca} - \Delta\phi_{eq,an} \quad (2.72)$$

$$E_{eq,an}^{tpb} = E_{eq,an}^{bulk} - \eta_{conc,an} \quad (2.73)$$

$$E_{eq,ca}^{tpb} = E_{eq,ca}^{bulk} - \eta_{conc,ca} \quad (2.74)$$

$$\eta_{act,an} = E_{eq,an}^{tpb} - E_{an} \quad (2.75)$$

$$\eta_{act,ca} = E_{eq,ca}^{tpb} - E_{ca} \quad (2.76)$$

$$E_{an} = E_{eq,an}^{bulk} - \eta_{act,an} - \eta_{conc,an} \quad (2.77a)$$

$$E_{ca} = E_{eq,ca}^{bulk} - \eta_{act,ca} - \eta_{conc,ca} \quad (2.78a)$$

$$E_{cell} = E_{an} - E_{ca} - \eta_{ohm} \quad (2.79a)$$

$$E_{cell} = E_{rev}^{bulk} + (\eta_{act,ca} + \eta_{conc,ca}) - (\eta_{act,an} + \eta_{conc,an}) - \eta_{ohm} \quad (2.80)$$

$$E_{rev}^{bulk} = E_{eq,an}^{bulk} - E_{eq,ca}^{bulk} \quad (2.81)$$

Taking into account the above definitions for electric potential differences, one sees that E may be identified as the so-called “electrode oxidation potential” (E_{oxi}), which is associated with the oxidation half-reaction of that electrode:

$$E_{an} = E_{an,oxi} = -\Delta\phi_{eq,an} = -E_{an,red} = -\left(\phi_e^{tpb} - \phi_{O_2}^{tpb}\right)_{an} \quad (2.77b)$$

$$E_{ca} = E_{ca,oxi} = -\Delta\phi_{eq,ca} = -E_{ca,red} = -\left(\phi_e^{tpb} - \phi_{O_2}^{tpb}\right)_{ca} \quad (2.78b)$$

Using Eq. (2.79a) and ignoring ohmic losses, one obtains

$$E_{cell} = E_{an,oxi} - E_{ca,oxi} = E_{an,oxi} + E_{ca,red} \quad (2.79b)$$

This is a well-known equation in which the potentials of the half-cells are added to get the overall standard cell potential (EMF) of an electrochemical cell. Thus $\Delta\phi_{eq}$ is identified, in the case of criteria and conventions used in this work, as the “electrode reduction potential” (E_{red}) associated with the reduction half-reaction of the considered electrode, at equilibrium.

More specifically on what concerns Eq. (2.66), published papers in SOFC literature usually assume that, in equilibrium situations, the condition $a_{O_2,tpb,ca}^\times = a_{O_2,tpb,an}^\times$ is always verified. For such condition to be true, the following assumptions should (at least approximately) hold:

- i. The chemical potential of oxygen ions ($\mu_{O^{2-}}$) should be constant throughout the electrolyte thickness. That is, the concentration of charge carriers is “high enough” so that there is no material composition variation along this phase^[87]; and the electrolyte phase should be also free of meaningful temperature gradients.
- ii. The equilibrium chemical activity of oxygen ions, at the TPBs on both sides (anode and cathode), should not depend on the nature of the adjacent gas atmosphere (both contact chemistry and space charge zone), as will be discussed in §§3.3.2.

Based on the above considerations, the following simplified expression is more commonly found in the literature (the subscripts “an” and “ca” were omitted for simplicity):

$$\Delta\phi_{eq,ca}^{tpb} - \Delta\phi_{eq,an}^{tpb} = -\frac{\Delta G^\ddagger}{2F} - \frac{RT}{2F} \ln \left(\frac{a_{H_2O,tpb}}{a_{H_2,tpb} \sqrt{a_{O_2,tpb}}} \right) \quad (2.82)$$

2.3.2 Macroscopic Calculation of Activation Polarization

As presented in §§2.3.1, the physical origin of potential step ($\Delta\phi$) is the electric potential difference through surface shells that contain excess electric charges and oriented dipoles. In SOFCs, these surface shells form at solid/solid (grain boundary) interfaces wherein electrochemical charge-transfer reactions take place, locally interconverting ionic and electronic currents to and from those solid phases (see Fig. 2.7). More precisely, the charge-transfer is related to the surface potential difference between the inner potential of electrode (ϕ_{elde}) and the inner potential of electrolyte (ϕ_{elyt}). As the charge carrier, inside the ionic phase (oxide ion) or electronic phase (electron), approaches the solid/solid interface, it encounters a steep potential cliff ($\Delta\phi$) that ultimately drives the emission current through the phase boundary (*i.e.*, the number of charges jumping out of or striking a unity area of surface per unit time). Thus, electrochemical kinetics is a function of $\Delta\phi$, which in the anode case, for example, can be expressed in a local form as (see Eq. (2.59)):

$$\Delta\phi_{an}(\vec{r}, i) = \phi_{an}(\vec{r}, i) - \phi_{elyt}(\vec{r}, i) \quad (2.83)$$

When a finite current density flows through the SOFC composite electrode⁸, coupled processes (see Fig. 2.7) such as ionic conduction, electronic conduction, electrochemical

⁸ As described in **Chapter 1**, oxygen ions are conducted in the “electrolyte phase” (*e.g.*, *YSZ*) and electrons in the “electronic phase” (*e.g.*, *Ni*) of a SOFC composite electrode.

reactions, and the transport of gas-phase species lead to a spatial distribution of inner potentials ϕ within the considered phases. This spatial distribution occurs mainly along the thickness of the electrode^[7, 8, 13], if the problem is assumed one-dimensional, *i.e.* $\phi = \phi(z)$, as it is illustrated on Fig. 2.7.

Figure 2.7: schematic depiction of a reaction mechanism (hydrogen spillover) of charge-transfer at the TPB (electrode, electrolyte, and gas phases) of a SOFC composite anode. Shown is the case of a purely ionic conducting electrolyte and purely electronic conducting electrode (figure by the author based on the description from [72]).

The goal is to obtain one possible set of governing equations and closure relations for the processes (transport and reaction) occurring on solid phases, so that $\Delta\phi_{an}$ and current densities can be related to one another. In the analysis that follows, the contribution of the gas-phase to this relation will be restricted to the Butler–Volmer and Nernst phenomenological formalisms. When deriving the set of equations, one will not be concerned in mapping out the region of validity of the model (such as their eventual limitation to near-equilibrium conditions). This type of analysis is echoed by other references elsewhere in the literature^[8, 87, 69, 88, 89, 90].

The current density i (A cm^{-2}) in Eq. (2.83) is the one measured at the anodic and cathodic current collectors (*i.e.*, the current that actually circulates around the outer circuit of SOFC). It is the sum of the Faradaic current i_F due to charge-transfer reactions and the current i_{dl} due to the charging and discharging of electric double layers upon voltage transients. Considering three-dimensional electrodes, the total current i_T (A) follows from integration over the spatially varying volumetric values (volume-specific densities) of these currents, i_F^{V} and i_{dl}^{V} (A cm^{-3}):

$$i_T = \int_{\text{V}} (i_F^{\text{V}} + i_{dl}^{\text{V}}) d\text{V} \quad (2.84)$$

For two-dimensional (flat) electrodes, area-specific values are used. In this case, i_T is integrated over one specific spatial coordinate. If one assumes that $\phi = \phi(z)$, then

$$i = i_{\partial\mathbb{V}} = i_F^{\partial\mathbb{V}} + i_{dl}^{\partial\mathbb{V}} = \int_{z=0}^{\delta_{an}} (i_F^{\mathbb{V}} + i_{dl}^{\mathbb{V}}) dz \quad (2.85)$$

Where $i_{\partial\mathbb{V}}$ is the total current per unit area normal to the z direction (*i.e.*, the cell current density); $i_F^{\partial\mathbb{V}}$ and $i_{dl}^{\partial\mathbb{V}}$ are the faradaic and double-layer currents flowing per unit area of the boundary of the electrode in the z direction; and δ_{an} is the thickness of the porous anode. If the electric double-layer behaves as an ideal capacitor, i_{dl} may be evaluated as^[67]

$$i_{dl}^{\partial\mathbb{V}} = i_{dl}^{\partial\mathbb{V}}(t) \propto \frac{\partial(\Delta\phi)}{\partial t} \quad (2.86)$$

This $i_{dl}^{\partial\mathbb{V}}$ current can alter the total electric current upon transient changes of the potential step $\Delta\phi$. However, under “macroscopic steady-state conditions” one normally assumes that the potential step is time-invariant within the characteristic time scale of our problem, and thus the RHS of Eq. (2.86) vanishes. Thus,

$$\frac{\partial(\Delta\phi)}{\partial t} = 0 \quad \Rightarrow \quad i = i_F^{\partial\mathbb{V}} = \int_{z=0}^{\delta_{an}} (i_F^{\mathbb{V}}) dz \quad \text{and} \quad i_T = \int_{\mathbb{V}} (i_F^{\mathbb{V}}) d\mathbb{V} \quad (2.87)$$

To calculate the local ionic current density $i_{io}(z)$ of the electrolyte phase, the following assumptions are also made: (i) the concentration of charge carriers is high enough so that there is no material composition variation along the phase; and (ii) the phase is free of meaningful temperature gradients. With such assumptions, one can say that there are no noticeable changes in the chemical potential of oxide ions and hence the electrical field remains as the dominant driving force within the electrolyte (see also §§3.3.1). Therefore, after applying the Nernst-Einstein equation^[87], one obtains

$$i_{io}(z) = -\sigma_{io}^{\text{eff}} \nabla \phi_{elyt} = -\sigma_{io}^{\text{eff}} \frac{\partial \phi_{elyt}}{\partial z} \quad (2.88)$$

where σ_{io}^{eff} is an effective ionic conductivity. Clearly, Eq. (2.88) is a statement of Ohm’s law. In the SOFC literature it is said at times^[91] that this equation refers to the so-called perfect ionic conductor. However, this assertion is an antinomy because in perfect conductors $\nabla \phi \rightarrow 0$ for interior points (*i.e.*, space charge density is zero). Then, considering the continuity equation for electric charges under steady-state condition^[92]

$$\nabla \cdot \mathbf{i} = 0 \quad \Rightarrow \quad \nabla \cdot (\mathbf{i}_{io} + \mathbf{i}_e) = -i_F^{\mathbb{V}} + i_F^{\mathbb{V}} \quad (2.89)$$

The one-dimensional spatial derivative of the ionic current is thus given by

$$\frac{\partial i_{io}}{\partial z} = -i_F^{\mathbb{V}} \quad (2.90)$$

In Eq. (2.90) i_F^V is a volumetric source term (generally denoted by $\dot{S}_{V,\phi}$), which represents local electrochemical reactions at TPB (e.g., see Eq.(2.111)). Combining Eq. (2.88) and (2.89) yields

$$\nabla \cdot (-\sigma_{io}^{eff} \nabla \phi_{elyt}) = \frac{\partial}{\partial z} \left(-\sigma_{io}^{eff} \frac{\partial \phi_{elyt}}{\partial z} \right) = -i_F^V \quad (2.91)$$

As the electrolyte (ionic) conductivity is typically several orders of magnitude lower than the electrode (electronic) conductivity, one may assume that the latter has a constant electric potential ϕ_{an} , that is, it behaves as an “ideal conductor” when compared to electrolyte (see further discussion in §§2.3.3):

$$\frac{\partial \phi_{an}}{\partial z} = 0 \quad (2.92)$$

Thus from Eq. (2.83)

$$\frac{\partial(\Delta\phi_{an})}{\partial z} = \frac{\partial(\phi_{an} - \phi_{elyt})}{\partial z} = -\frac{\partial\phi_{elyt}}{\partial z} \quad (2.93)$$

Substituting Eq. (2.93) in Eq. (2.91) one finally obtains

$$\frac{\partial}{\partial z} \left(\sigma_{io}^{eff} \frac{\partial(\Delta\phi_{an})}{\partial z} \right) = -i_F^V \quad (2.94)$$

which is the (one-dimensional) macroscale-continuum governing equation for the spatial distribution of potential step $\Delta\phi$ through the thickness of a composite anode.

Now we turn our attention to the phenomenological relation between $\Delta\phi$ and electrochemical reactions, in the light of chemical kinetics. In other words, here one seeks to obtain a clear, although succinct, view on the derivation of Butler-Volmer-based electrode kinetics, so that one could finally link this relation with the definition of activation polarization, Eq. (2.40) and Eq. (2.41). Consider the following elementary step of a heterogeneous reaction^[87]:

In which species A can change its nature and/or its position. If $A \equiv B$, a pure transport step is being described. If $A \not\equiv B$ but conversely $y = y'$ can be assumed (or if differences in the position coordinate are unimportant), a homogeneous reaction is being addressed. Here y is the coordinate axis normal to the solid/solid interface wherein the electrochemical charge-transfer reaction takes place, that is, it is the normal direction to the surface shell through which the potential difference ($\Delta\phi$) develops (the “gray plane” in Fig. 2.7). Thus, Δy represents the jump distance, or displacement, from ϕ_{elyt} to ϕ_{an} or vice-versa. For the archetype reaction

(2.95), the net flux J_{net} (composed of forward $\tilde{J}_A$ and backward $\tilde{J}_B$ contributions) of the particle number (n_i) passing from y to y' , in unit time, can be formulated as:

$$J_{net} = \tilde{J}_A - \tilde{J}_B = \tilde{k}_A n_A(y) - \tilde{k}_B n_B(y') \quad (2.96)$$

During this process the particles may or may not change their nature. The term J_{net} might be acknowledged as an analogous of net current density (i). In Eq. (2.96), k is a rate constant which is independent of the particle density, but exponentially dependent on the chemical barrier to be overcome^[33, 93]. For the forward jump one has:

$$\tilde{k} = k_0 \exp \left[-\tilde{\Delta G}^\ddagger / (\mathcal{R}T) \right] \quad (2.97)$$

The tilde indicates that the actual chemical barrier ($\tilde{\Delta G}^\ddagger$) is modulated by the electrical field $-\Delta\phi/\Delta y$, that is, the Gibbs energy profile of the electrochemical reaction is distorted by the energy step $z_e \mathcal{F} \Delta\phi$ according to^[87] (see also Fig. 2.8):

$$\tilde{\Delta G}^\ddagger - \overline{\Delta G}^\ddagger = \widetilde{\Delta_r G} = \Delta_r G - z_e \mathcal{F} (\phi(y') - \phi(y)) = \Delta_r G + z_e \mathcal{F} (\phi(y) - \phi(y')) \quad (2.98)$$

Figure 2.8: Gibbs energy profile of an electrochemical reaction (continuous line) that is distorted by the potential drop $\Delta\phi$ (dotted line). The activation energy for the forward reaction is increased by $\tilde{\alpha} z_e \mathcal{F} \Delta\phi$, whereas for the reverse reaction it is reduced by $(1 - \tilde{\alpha}) z_e \mathcal{F} \Delta\phi$ (figure by the author).

According to Fig. 2.8, the activation energy for the reaction from left to right (or right to left) is increased (or reduced) by $\tilde{\alpha} z_e \mathcal{F} \Delta\phi$ (or $\tilde{\alpha} z_e \mathcal{F} \Delta\phi$), where $\tilde{\alpha}$ and $\tilde{\alpha}$ are symmetry factors. On account of the applied field ($-\Delta\phi/\Delta y$), if $\tilde{\alpha} \neq 1 - \tilde{\alpha}$ the barrier is no longer symmetrical. Thus,

$$J_A = n_A(y) k_0 \exp \left[-\tilde{\Delta G}^\ddagger / (\mathcal{R}T) \right] = n_A k_0 \exp \left[-(\overline{\Delta G}^\ddagger + \tilde{\alpha} z_e \mathcal{F} \Delta\phi) / (\mathcal{R}T) \right] \quad (2.99)$$

$$J_B = n_B(y) k_0 \exp \left[-\overline{\Delta G}^\ddagger / (\mathcal{R}T) \right] = n_B k_0 \exp \left[-(\overline{\Delta G}^\ddagger - (1 - \tilde{\alpha}) z_e \mathcal{F} \Delta\phi) / (\mathcal{R}T) \right] \quad (2.100)$$

At thermodynamic equilibrium, it is noted that the forward and reverse fluxes must balance, so that there is no net flux ($J_{net} = 0$). Thus, in the case depicted by Eq. (2.98) and Fig. 2.8, the “buildup of interfacial potential” $\phi(y') - \phi(y)$ seeks to equalize such unbalanced situation, where the forward rate was (initially) faster than the reverse rate, due to unequal

activation barriers for the forward in comparison to reverse reaction (*i.e.*, lower Gibbs energy of the product state compared to reactant state). The equalization occurs by increasing the forward activation barrier from $\overrightarrow{\Delta G}^\ddagger$ to $\overrightarrow{\Delta G}$, while decreasing the reverse activation barrier from $\overleftarrow{\Delta G}^\ddagger$ to $\overleftarrow{\Delta G}$. Writing the forward and reverse density fluxes at equilibrium:

$$J_{A,eq} = n_{A,eq}(y) k_0 \exp \left[-\overrightarrow{\Delta G}_{eq}^\ddagger / (\mathcal{R}T) \right] \quad (2.101)$$

$$J_{B,eq} = n_{B,eq}(y') k_0 \exp \left[-\left(\overleftarrow{\Delta G}_{eq}^\ddagger - \Delta_r G^\ddagger - z_e \mathcal{F} (\phi(y) - \phi(y'))_{eq} \right) / (\mathcal{R}T) \right] \quad (2.102)$$

$$J_{A,eq} = J_{B,eq} = J_0 \quad (2.103)$$

Thus, from Eq. (2.101), (2.102), and (2.103) one obtains

$$(\phi(y) - \phi(y'))_{eq} = \Delta\phi_{eq} = -\frac{\Delta_r G^\ddagger}{z_e \mathcal{F}} - \frac{\mathcal{R}T}{z_e \mathcal{F}} \ln \left(\frac{n_{B,eq}(y')}{n_{A,eq}(y)} \right) \quad (2.104)$$

Compare this result with Eq. (2.45) and (2.47). Still considering equilibrium conditions, the forward and reverse reactions may now be expressed in function of J_0 :

$$\begin{aligned} J_{A,eq} &= n_{A,eq} k_0 \exp \left[-\overrightarrow{\Delta G}_{eq}^\ddagger / (\mathcal{R}T) \right] \\ &= n_{A,eq} k_0 \exp \left[-\overrightarrow{\Delta G}^\ddagger / (\mathcal{R}T) \right] \exp \left[-(\tilde{\alpha} z_e \mathcal{F} \Delta\phi_{eq}) / (\mathcal{R}T) \right] = \\ &= J_0 = \tilde{J}_0 n_{A,eq} \end{aligned} \quad (2.105)$$

$$\text{Where } \tilde{J}_0 = k_0 \exp \left[-\overrightarrow{\Delta G}^\ddagger / (\mathcal{R}T) \right] \exp \left[-(\tilde{\alpha} z_e \mathcal{F} \Delta\phi_{eq}) / (\mathcal{R}T) \right]$$

$$\begin{aligned} J_{B,eq} &= n_{B,eq}(y') k_0 \exp \left[-\left(\overleftarrow{\Delta G}_{eq}^\ddagger - \Delta_r G^\ddagger - z_e \mathcal{F} (\phi(y') - \phi(y))_{eq} \right) / (\mathcal{R}T) \right] \\ &= n_{B,eq} k_0 \left(\frac{n_{A,eq}}{n_{B,eq}} \right) \exp \left[-\overrightarrow{\Delta G}^\ddagger / (\mathcal{R}T) \right] \exp \left[-(\tilde{\alpha} z_e \mathcal{F} \Delta\phi_{eq}) / (\mathcal{R}T) \right] \\ &= J_0 = \tilde{J}_0 n_{B,eq} \left(\frac{n_{A,eq}}{n_{B,eq}} \right) \end{aligned} \quad (2.106)$$

Combining Eq. (2.105) with (2.99), and Eq. (2.106) with (2.100), yields

$$J_A = J_0 \left(\frac{n_A(y)}{n_{A,eq}} \right) \exp \left[-(\tilde{\alpha} z_e \mathcal{F} (\Delta\phi - \Delta\phi_{eq})) / (\mathcal{R}T) \right] \quad (2.107)$$

$$J_B = J_0 \left(\frac{n_B(y')}{n_{B,eq}} \right) \exp \left[((1 - \tilde{\alpha}) z_e \mathcal{F} (\Delta\phi - \Delta\phi_{eq})) / (\mathcal{R}T) \right] \quad (2.108)$$

Substituting Eq. (2.40), Eq. (2.107), and (2.108) in Eq. (2.96) one obtains the relation between the net particle flux density and the electric potential step:

$$\begin{aligned} J_{net} &= J_0 \left\{ \frac{n_A}{n_{A,eq}} \exp[-\tilde{\alpha} z_e \mathcal{F} (\Delta\phi - \Delta\phi_{eq})/(\mathcal{R}T)] - \frac{n_B}{n_{B,eq}} \exp[(1 - \tilde{\alpha}) z_e \mathcal{F} (\Delta\phi - \Delta\phi_{eq})/(\mathcal{R}T)] \right\} \\ \Rightarrow J_{net} &= J_0 \left\{ \left(\frac{n_A}{n_{A,eq}} \right) \exp[-\tilde{\alpha} z_e \mathcal{F} \Delta\phi_{act}/(\mathcal{R}T)] - \left(\frac{n_B}{n_{B,eq}} \right) \exp[(1 - \tilde{\alpha}) z_e \mathcal{F} \eta_{act}/(\mathcal{R}T)] \right\} \end{aligned} \quad (2.109)$$

Equation (2.109) is a direct result of conditions imposed by Eq. (2.98), (2.99), and (2.100) (as per Fig. 2.8), which all together represent a reduction reaction. Or, to say it correctly, considering Eq. (2.96) in which A is the reactant being depleted and that by making $\Delta\phi$ more negative favors the forward jump, this implies that A is reduced while in the reverse jump B is oxidized. The derivation of an alternative expression for J_{net} in the case that Eq. (2.96) is an oxidation reaction can be handled in a completely analogous fashion.

One should note that the faradaic current in the cathodic half-cell has an opposite sign of that in the anodic half-cell, thus the resulting sign of J_{net} must be consistent in each of the half-cells. This is particularly important for equations in which J_{net} (or equivalently, $i_F^\forall$) is incorporated as a source term, e.g., as in Eq. (2.90). Therefore, the above derivation procedure employs sign conventions and requires thermodynamic consistency. That is why in calculating the relationships between activation energies, Gibbs energy, overvoltages, and so forth, it is indispensable that signs are properly accounted for. More specifically, in the case of the Butler–Volmer equation (BVE), there is usually a certain convention in writing Eq. (2.109), regardless if the half-cell reaction is taking place at the cathode or anode. The forward reaction is an anodic process and the backward reaction is a cathodic process (at a given electrode):

$$i \stackrel{\text{def}}{=} i_{an} - i_{ca} = i_0 \{ \exp[\alpha_a z_e \mathcal{F} \eta_{act}/(\mathcal{R}T)] - \exp[-\alpha_c z_e \mathcal{F} \eta_{act}/(\mathcal{R}T)] \} \quad (2.110)$$

By way of example, and so to complete the set of equations that governs the spatial distribution of potential steps $\Delta\phi$ (Eq. (2.94)), consider the following semi-empirical BVE used to calculate $i_F^\forall$ (which, in this case, represents the current density per unit of TPB length) in a Ni/YSZ anode^[91]:

$$i_F^\forall = i_0^{TPB}(z) \lambda_{tpb}(z) \{ \exp[2 \mathcal{F} \eta_{A,an}(z)/(\mathcal{R}T)] - \exp[-\mathcal{F} \eta_{A,an}(z)/(\mathcal{R}T)] \} \quad (2.111)$$

Where λ_{tpb} (a morphological parameter) is the TPB length per unit volume of the porous electrode (e.g., $\mu\text{m}/\mu\text{m}^3$); and i_0^{TPB} (current per unit of TPB length) is the exchange current density fitted from patterned-electrode experiments^[94] according to

$$i_0^{TPB} = 31.4 (p_{H_2}(z)/p_{ref,H_2})^{-0.03} (p_{H_2O}(z)/p_{ref,H_2O})^{0.4} \exp[-1.52 \times 10^5/(\mathcal{R}T)] \quad (2.112)$$

Based on the above examination it is seen that the local activation polarization, $\eta_{act}(z)$, “is free” of effects beyond those directly related to the electrochemical reaction very near a narrow region around the TPB site (e.g., charge-transfer reaction, local concentration-induced

losses, and local interfacial transport phenomena). Furthermore, within the BVE formalism, $\Delta\phi$ possess only macroscopic coherence (*i.e.*, a “non-equilibrium surface potential difference” between the bulk of electrode and electrolyte), thereby ignoring its fundamental relation with the energy states of charge carriers and hiding most of the details about the electric boundary-layer formed at the solid/solid interface. Phenomenological semi-empirical models such as Butler–Volmer kinetics seem to achieve good results under certain circumstances, despite their inherent “macroscopic degeneracy”^[87,67,75]. In some situations, however, improved physical fidelity is required to correctly describe the mechanism of electrode overvoltage^[75,71].

In order to have a deeper insight into the relation between $\Delta\phi$ and the net current, it would be necessary to model the electron exchange processes at the phase boundary. When electrons flow (*i.e.*, when an electronic current is established), the energy conservation implies that there must be an interfacial electric field (that is, a potential difference between the two bulk phases at their interface) that does the work on the transmitted electron. This work (which is proportional to $\Delta\phi$ on the “microscale”) is the difference of the work function associated with the extraction of an electron from a molecule and the work function gained by inserting the electron to the solid conductor, or vice-versa^[95]. The appreciation of this process (namely, the interaction between charge carriers and bulk materials) can be accomplished using models such as those from Thomas-Fermi theory^[96, 97] and molecular electronics^[98, 99]. From the perspective of these models, $\Delta\phi$ is a potential bias that appears as the difference between the local Fermi-energies (or, somewhat equivalently, between macroscale-continuum electrochemical potentials) on the electrode and electrolyte sides. As long as the potential bias between the two sides is maintained, current will flow through the system as the molecule tries (and fails) to reach equilibrium with both junctions. When $\Delta\phi$ is positive (that is, when the Fermi energy on the electrode is lower than on the electrolyte), electrons will flow from the electrolyte to the electrode (accordingly, in this case, the current will flow from electrode to the electrolyte and its value is defined as being negative). Conversely, when $\Delta\phi$ is negative, electrons will flow from the electrode to the electrolyte. This result endorses the definitions given by Eq. (2.40) and (2.41) in §§2.3.1.

2.3.3 Active Layer, Penetration Depth, and Perfect-Electronic-Conductors

In the traditional design of SOFC anodes and cathodes (*e.g.*, *Ni-YSZ* and *LSM-YSZ* composites, respectively), electrochemical reactions do not occur through the entire electrode layer. On the contrary, these reactions are concentrated in a reactive region that is thinner than the anode (or cathode) total thickness^[100, 101], closer to the electrolyte side. This region (of the

order of 10-30 μm) is called the active layer of electrode (see Fig. 2.9), wherein large portion of the ionic current (i_{io}) is exchanged to electronic current (i_e). As will be examined in detail in §§4.3.1 (and also in **APPENDIX A**), a simplified mathematical model of gas-diffusion electrodes can be developed to investigate the qualitative effects of mass-transport limitations on the polarization characteristics within this active layer zone (see Fig. 2.10), when one considers the “limiting situations” of ideal ionic transport or ideal mass transport of feed-gas.

Figure 2.9: three-dimensional (simulated) current streamline distributions in a anode ($\text{Ni} - \text{YSZ}$) microstructure. Red color and blue color represent, respectively, ionic and electronic currents (figure reproduced from [102]).

Considering the example of an anode according to Fig. 2.10, oxide ions come from the electrolyte (left side), whereas gas molecules arrive from the anode outer layer (right side). The conversion reaction consumes neutral gas molecules, and produces currents of electrons and oxide ions. The feed gas concentration (C_{fg}) decreases towards the electrolyte, whereas the electronic current (i_e) grows and ionic current (i_{io}) decays with the distance from electrolyte interface. The conversion is assumed to occur in an idealized slab (active layer) of thickness l_t : on the right side of this slab, i_{io} is zero and i_e reaches the value of the total cell current density (i); accordingly, i is equal to i_{io} at the electrolyte interface. The driving force for electrochemical conversion is, in this case, provided by the local “augmented” polarization $\eta = \eta(z)$; the voltage required to completely convert i , from ionic into electronic form, is η_0 . The cell polarization curve of this active layer is then given by $\eta_0 = \eta_0(i)$.

Figure 2.10: active layer schematics with profiles of ionic (i_{io}) and electronic (i_e) current densities, feed gas concentration (C_{fg}), local augmented polarization ($\hat{\eta}$), overall cell polarization ($\hat{\eta}_0$), and the cell current density (i). (figure by the author).

As will be seen in §§4.3, §§4.4, and §§4.5, when the modeling study disregards the details of what happens within the active layer (a simplification that is frequently applied in the literature), this layer is approximated by an effective zero-thickness model and, in this case, proper boundary conditions are prescribed. In practical terms, this means that there is the assumption of a zero-dimensional surface reaction and thus the layer is treated as an idealized zero-thickness surface, which has mass sources/sinks term coupled to the neighboring electrode phase. Be that as it may, this reduced model does the same job of current-to-current conversion, “encapsulating” the description of electrochemical reactions. Whichever model is used, the judgment for the spatial limits of an active layer is essentially arbitrary without the availability of experimental data on local parameters and/or properties.

It is worthwhile to clarify that there are “imprecisions”⁹ in the way in that polarization is loosely defined in several works from the SOFC literature, leaving unclear the exact definitions of activation polarization, concentration (diffusional) polarization, and “total” polarization. The strict definition of a polarization depends on the chosen electric potential reference and on the attribution of an equilibrium cell potential^[67]. Furthermore, there is an apparent indifference (mainly in terms of nomenclature) between local polarization and “total” polarization, where the latter could be the total (integrated) activation polarization or the sum of diffusional and activation polarizations (*i.e.*, “augmented polarization”). For these reasons, a number of explanations are included in the present monograph (especially in section §§2.3). This addendum proves necessary to conceptual consistency of further developments (It is fair to

⁹ Here it is best to use the term “imprecision”, because the definition of different types of polarizations is usually done at the discretion of the researcher. Thus, for one to coin such careless treatment as “an error” would be, strictly speaking, exaggerated. On the other hand, however, the application of “careless definitions” can indeed constitute potential sources of errors in subsequent mathematical derivations (see **Chapter 4**).

say that the correction of a “flawed assertion” often requires more space than is taken up in setting forth the incorrectness). Ultimately, such addendum also allows one to bring up aspects that are rarely vetted in the SOFC modeling literature, such as the careless definition of “activation polarization” and “augmented polarization” and how their misleading definitions might affect the modeling of transport phenomena within the gas phase and the ensuing effects on cell performance (e.g., concentration-induced voltage losses).

Being acute on certain electrochemical concepts allows one to stress awareness of the limits of models herein studied and developed. However, electrochemical modeling assumptions and their limitations are not thoroughly scrutinized in this work. The objective herein is solely to clarify immediate inconsistencies that could compromise the fullest comprehension of a given mathematical model in the next chapters of this work, which are pertinent to the modeling of gas-phase transport processes.

At first glance, and without imposing any prior assumption concerning the concrete case under study, electrochemical reaction rates are not evenly distributed within the active layer of an electrode^[67]. In fact, in the absence of non-ohmic polarization (that is, when E_{cell} is independent of $\nabla \cdot \mathbf{i}_{io}$ and of reacting species concentration), the reaction occurs only at the boundaries of the active layer and, to minimize the ohmic potential drop, the total current density (i) tends to immediately divide between the ionic phase (i_{io}) and electronic (i_e) phase in proportion to their effective conductivities^[67]. This would require, first, that extremely high reaction rates exist near the interfaces $z = 0$ and/or $z = l_t$ (see Fig. 2.10), thereby leading to the aforementioned nonuniform reaction distribution, as described in the above paragraphs and which seems to be the ordinary situation in SOFCs. Thus, in this limiting case, the reaction rate at the electronic-ionic interface would be proportional to $i\sigma_e/(\sigma_e + \sigma_{io})$ and the current entering the composite electrode would immediately distribute itself between both phases, so that in each phase the ohmic drop is the same. On the other hand, slow electrode reaction kinetics “forces” the reaction to be more uniformly distributed so to reduce the local transfer current (i_F^{∇}). In this sense, the effect of activation polarization is to distribute the reaction more uniformly through the electrode. For instance, if reactive TPBs are sparsely distributed along the composite electrode, instead of being concentrated near the boundaries, then electrons will have a wider distribution of percolating paths. As a result, the ionic current would also need to diffuse farther from the electrolyte to the current collector side, through a less conductive (“longer”) YSZ network, thus increasing ohmic losses. These competing effects of ohmic potential drop and slow reaction kinetics determine the resulting distribution. Figure 2.11 shows an idealized equivalent circuit of the composite electrode illustrating the current flowing

through the ionic and electronic resistances, and the current transfer from one phase to the other (*i.e.*, electrochemical reaction).

Figure 2.11: electric analog of a composite electrode with ohmic resistances representing electronic and ionic phases (upper and lower horizontal resistors), and kinetic resistances (vertical elements) representing electrochemical reactions. Vertical branches also have elements representing the cell potential $\Delta\phi_{eq}^{tpb}$ (figure modified from [67]).

For the problem in the active layer, specifically, five dimensionless ratios govern the current distribution^[103]. These can be stated as: a dimensionless current density ($\hat{l}_\delta$); a dimensionless exchange current density ($\hat{l}_v$); the ratio α_a/α_c of the transfer coefficients in the BVE; the ratio σ_{io}/σ_e of the effective conductivities of the ionic and electronic phases; and an additional dimensionless parameter ($\hat{l}_q$) that indicates the effect of mass transport of the reacting molecular species on the steady-state reaction distribution (*i.e.*, the magnitude of the electrochemical consumption rate relative to the mass-transfer rate).

$$\hat{l}_\delta = \frac{\alpha_a z_e \mathcal{F} i l_t}{\mathcal{R}T} \left(\frac{1}{\sigma_{io}} + \frac{1}{\sigma_e} \right) \quad (2.113)$$

$$\hat{l}_v^2 = (\alpha_a + \alpha_c) \frac{z_e \mathcal{F} i_*^\vee l_t^2}{\mathcal{R}T} \left(\frac{1}{\sigma_{io}} + \frac{1}{\sigma_e} \right) \quad (2.114)$$

$$\hat{l}_q = i l_t / (z_e \mathcal{F} D C_{ref}) \quad (2.115)$$

where $i_*^\vee$ is a “reference” exchange current density (see §§2.3.4 for its precise definition); D is a reference (or scaling) gas diffusion coefficient of the gas mixture; and C_{ref} is a reference (or scaling) molar gas concentration. The other parameters are as described in previous pages.

Therefore, the current and reaction distributions along the depth of the electrode may be described through use of these dimensionless parameters, indicating that distributions are influenced by the type of activation polarization, by mass transport of the reacting species, and finally by the effective conductivities of the two phases (ionic and electronic). Furthermore, the distance to which the reaction can penetrate the composite electrode determines how thick an

electrode can be effectively utilized (*i.e.*, it determines the thickness of active layer). Thus, electrodes much thicker than this penetration depth are not fully utilized.

In the absence of concentration effects, the nonuniformity of reaction distribution is determined by the parameters $\hat{l}_\delta$ and $\hat{l}_v^2$ [67]. They express the ratios of the competing effects of ohmic losses and slow electrodes kinetics. For small values of either $\hat{l}_\delta$ and $\hat{l}_v^2$, the reaction is uniform (see Fig 2.12). For large values of either $\hat{l}_\delta$ and $\hat{l}_v^2$, the ohmic effect dominates and the reaction distribution is mostly nonuniform (reaction occurs mainly at the active layer/electrolyte interface). The appearance of the ratio α_a/α_c inside these parameters is a direct consequence of applying the Butler–Volmer formalism, but its role is difficult to discern. For small values of σ_{io}/σ_e , reaction occurs preferentially near the active layer/electrolyte boundary at the expense of the region near the outer electrode layer (see Fig. 2.12). This ratio σ_{io}/σ_e serves to shift the reaction from one boundary to the other so that the reaction is somewhat more uniform as σ_{io} approaches σ_e , at constant $\hat{l}_\delta$ (see figures 2.12 and 2.13). If both conductivities are non-zero, the ohmic contribution to the voltage drop will eventually dominate at high current values. If one phase has a much higher conductivity in comparison to the other, a double Tafel slope results [104].

Figure 2.12: Reduced current distributions for Tafel polarization: (a) with $\sigma_{io} \rightarrow +\infty$; and (b) with $\sigma_e \rightarrow +\infty$. Simulation results obtained using the model proposed by Newman and Tobias^[103], where $\hat{l}_{io} = i_{io}/i$.

Figure 2.13: Reduced current distributions for Tafel polarization: (a) $\sigma_{io} = \sigma_e$; and (b) for different σ_{io}/σ_e ratios. Simulation results obtained using the model proposed by Newman and Tobias^[103], where $\hat{l}_{io} = i_{io}/i$.

In the study developed by Newman and Tobias^[103], the parameter $\hat{l}_\delta$ was used for the Tafel regime or conversion domain (high polarization). These authors have shown that at high current levels (with Tafel kinetics), $l_t/\hat{l}_\delta$ is the length that is more characteristic of the penetration of the reaction, and that the reaction distribution is independent of the exchange current density i_* . However, in the limit approached at low current densities, the nonuniformity of the reaction increases with increasing values of the parameter $\hat{l}_v^2$. Within the Tafel range, the authors also found that the relationship between these parameters of nonuniformity could be expressed as

$$\hat{l}_v^2 = \hat{l}_\delta \quad (2.116)$$

and thus,

$$\frac{l_t}{\hat{l}_v} = \left(\frac{RT \sigma_{io} \sigma_e}{(\alpha_a + \alpha_c) i_*^\nabla z_e \mathcal{F} (\sigma_{io} + \sigma_e)} \right)^{1/2} \quad (2.117)$$

Thus, for uniform concentration, Eq. (2.117) tells us that the reaction distribution becomes less uniform as one increases the: (i) magnitude of the current density; (ii) the thickness of the active layer; or (iii) the sum of the effective resistivities of the two phases. In any case, the point of most even distribution will not occur at zero current density unless $\alpha_a = \alpha_c = 1/2$ ^[103].

In the case when there are meaningful concentration gradients of reacting species, the steady-state reaction distribution will be shifted more or less strongly towards the active

layer/outer layer interface as a result of hindered movement of the incoming species (see §§4.3.1). When the diffusive transport of reactants/products controls the overall rate of electrochemical conversion, other factors will determine the “useful” thickness of the active layer. For instance, for large anodic polarizations, the penetration depth becomes equal to $l_t/\hat{l}_\alpha$ (see Eq. (2.113)). However, if mass transfer, as well as the ohmic losses and the electrode kinetics have similar importance, then the overall rate of conversion will be a function of all involved penetration depths, Eq. (2.113) and (2.115). For example, this problem could be described by the following equations^[103], which somewhat combine these dimensionless penetration depths:

$$\begin{aligned}\frac{d^2 \hat{i}_{io}}{d\hat{z}^2} &= -\frac{d\hat{i}_{io}}{d\hat{z}} \left(\hat{l}_\delta \hat{i}_{io} - \epsilon_e + \frac{d \ln \hat{C}_{fg}}{d\hat{z}} \right), \\ \frac{d\hat{C}_{fg}}{d\hat{z}} &= \hat{l}_\rho (1 - \hat{i}_{io})\end{aligned}\quad (2.118)$$

where in Eq. (2.118), specifically,

$$\hat{i}_{io} = \frac{i_{io}}{i}, \quad \epsilon_e = \frac{l_t i}{\sigma_e b_{ts}} \quad (2.119)$$

and b_{ts} is the Tafel slope, which is defined as

$$b_{ts} = \frac{\mathcal{R} T}{\alpha \mathcal{F}}, \quad \text{with} \quad \alpha_a = \alpha_c = \alpha \quad (2.120)$$

The reaction penetration depth may be “measured” as either the thickness of the reaction zone near electrolyte interface, or as the thickness of the reaction zone starting near the outer-layer interface. Thus, l_t depends on which interface is taken as a reference and on the physics of the problem considered (e.g., diffusion-limited or conduction-limited).

Finally, to end this section, attention is driven to one of the more commonly implied assumptions in the SOFC literature, which considers the electronic phase of the composite electrode as a perfect conductor. Consequentially, for domain interior points one has

$$\begin{aligned}\nabla \phi_{elde} &\rightarrow 0 \\ \sigma_e \rightarrow +\infty &\Rightarrow \left(\frac{1}{\sigma_{io}} + \frac{1}{\sigma_e} \right) \rightarrow \frac{1}{\sigma_{io}}\end{aligned}\quad (2.121)$$

and recognizing that $\nabla \cdot \mathbf{i}_e$ remains a finite value. Such assumption is easily seen by comparing Eq. (2.114) with the following relation used in Kulikovsky’s model (examined in §§4.3.1):

$$\hat{l}_v^2 = \frac{2 i_*^\vee l_t^2}{\sigma_{io} b_{ts}} = \frac{2 a_s i_* l_t^2}{\sigma_{io} b_{ts}} \quad \text{where } a_s \text{ (cm}^2/\text{cm}^3\text{) is the specific area density of active electrocatalyst} \quad (2.122)$$

And taking into account the simplification proposed by Eq. (2.121). This assumption is equivalent to that made on the derivation of Eq. (2.92) and (2.93) in §§2.3.2.

As noted in §§2.3.2, in typical high-temperature SOFCs the electrolyte-phase conductivity is several orders of magnitude lower than the electrode-phase conductivity¹⁰. Thus, the condition given by Eq. (2.121) can be considered a very good approximation in macroscopic modeling (from Fig. 2.13b one verifies that when $\sigma_{io}/\sigma_e < 0.1$ (and $\hat{I}_\delta = 10$) the actual variation of the reaction rate profile is minimal). This is surely true for the bulk value of the conductivity, but one should acknowledge that the effective value of the electronic conductivity also depends on the microstructure features of the electron-conducting phase, howsoever large this bulk value may. These features might include the existence of internal contact resistances (e.g., heterogeneous grain boundaries) and the predominance of a poorly percolated conducting phase.

In any event, modern SOFC electrodes are sufficiently well designed to avoid low electronic conductivities due to inadequate microstructure features^[8]. However, during the course of SOFC life-time the composite electrode can suffer some form of microstructural degradation stemming from, for example, coarsening processes^[105, 106], but this possibility will not be discussed in this work.

2.3.4 Disambiguation of Activation, Concentration, and Augmented Polarizations

Here the focus is on the definition of η , i_*^∇ , and i (consequently, also of i_{io} and i_e). As will be found out, not only the clarification of these definitions is itself relevant, but rigorous definitions might as well identify problematic and undisclosed assumptions. The definition of η is in the lines of what has been discussed in §§2.2.2 (see Eq. (2.28)-(2.38)).

The form of the phenomenological BVE presents itself in several variations, whose number and type of parameters varies considerably (and somewhat inconsistently) in the literature. Compare, for instance, Eq. (2.109) with the following equation that is used in Kulikovsky's model (see §§4.3.1) and which expresses the decay of ionic current with z , at a rate given by Butler–Volmer electrode kinetics (RHS of the equation):

$$\frac{\partial i_{io}(z)}{\partial z} = -i_*^\nabla (C_{fg}/C_{ref})^a [\exp(\eta/b_{ts}) - \exp(-\eta/b_{ts})] = -2 i_*^\nabla (C_{fg}/C_{ref})^a \sinh(\eta/b_{ts}) \quad (2.123)$$

In Eq. (2.109) the concentration of reactants and products multiply each exponential factor separately, while in (2.123) only the reactant concentration is used, which multiplies both exponentials indistinctively. Thus, one may conclude that these equations are not directly comparable, even though both forms might be applied to model “the same problem”. For that

¹⁰ e.g., $\sigma_{io}^{eff} \cong 0.3 \text{ [S m}^{-1}\text{]}$ and $\sigma_e^{eff} \cong 4800 \text{ [S m}^{-1}\text{]}$, at $\cong 1000 \text{ [}^\circ\text{C]}$, for an anode made of porous *Ni/YSZ*^[8].

their parameters would need to be adjusted accordingly. In relation to Eq. (2.123), when it is said that the exponent “ α ” is the reaction order in respect to the feed gas, one must stress awareness about this statement. That is, this exponent is really a phenomenological parameter that does not necessarily have a formal kinetic meaning. It is, in the case of Eq. (2.123), a pseudo reaction order that “blends” the effects of both forward and reverse reactions. After having acknowledged this distinction, some comparisons are now put forth. Let R_{OR} (e.g., measured as $\text{mol cm}^{-3} \text{s}^{-1}$) be the electrochemical reaction rate expressed by

$$-R_{OR} = \frac{i_F^V}{z_e \mathcal{F}} = \frac{i_0^V}{z_e \mathcal{F}} [\exp(\eta/b_{ts}) - \exp(-\eta/b_{ts})] = k_0 C^\alpha [\exp(\eta/b_{ts}) - \exp(-\eta/b_{ts})] \quad (2.124)$$

where i_0^V (A cm^{-3}) is a volumetric exchange current density and k_0 (s^{-1}) is a reaction rate constant, which is independent of species concentration. From the equation above,

$$i_0^V = z_e \mathcal{F} k_0 C^\alpha \quad (2.125)$$

Comparing this result with Eq. (2.123), one verifies that

$$i_*^V = i_0^V (C/C_{ref})^{-\alpha} = z_e \mathcal{F} k_0 C_{ref}^\alpha \quad (2.126)$$

Meaning that i_*^V is an exchange current density evaluated at the concentration C_{ref} , which is thus not an arbitrary reference. Otherwise, the exponent “ α ” becomes only an experimentally-fitted parameter, which convey little or no physical meaning, just to satisfy Eq. (2.124).

In §§2.3.1 and §§2.3.2 it has been pointed out that the activation polarization η_{act} is function of the gas-phase composition (see Eq. (2.40), (2.41), (2.64), and (2.65)), but Kulikovsky and some other authors do not usually emphasize this point. The issue lies in what is the correct definition of “ η ” for what form of BVE. If an implicit approach is used, as per Eq. (2.35)-(2.39), the definition and hence the evaluation of η_{act} depends on $\Delta\phi_{eq}^{tpb}$, which is by its turn a function of the local gas composition and it accounts for local potential changes induced by local concentration effects. However, depending upon a different definition of “ η ” it can, however, also include effects due to non-local concentration losses, fact that could generate discrepancies if the modeling is not properly handled (see **Chapter 3**). Amongst the different polarizations (“ η ”) that are employed inside the exponentials terms of BVE, here follows the most common^[67]:

- The activation polarization “ η_{act} ”, which is defined as

$$\eta_{act} = \Delta\phi - \Delta\phi_{eq}^{tpb} = \phi_{elde} - \phi_{elyt} - \Delta\phi_{eq}^{tpb} \quad (2.127)$$

With $\Delta\phi_{eq}$ evaluated at the local (TPB) gas composition.

- And the “total” or augmented polarization “ η ”, which is defined as

$$\eta = \eta_{act} + \eta_{conc} = \phi_{elde} - \phi_{elyt} - \Delta\phi_{eq}^{ref} \quad (2.128)$$

With $\Delta\phi_{eq}^{ref}$ evaluated relative to a given reference electrode (e.g., defined at “bulk gas conditions”).

In Eq. (2.127), $\Delta\phi_{eq}^{tpb}$ is the open-circuit value of $\phi_{elde} - \phi_{elyt}$ at the prevailing gas composition on the surface of the pores (at TPBs). In Eq. (2.128), $\Delta\phi_{eq}^{ref}$ is the open-circuit value of $\phi_{elde} - \phi_{elyt}$ when the concentrations of the reactant and product are given at the some reference condition. Thus, in both these equations $\Delta\phi_{eq}$ is the value of the potential difference between the electrode and electrolyte at which the rate of the forward reaction equals the rate of the reverse reaction. In this situation, the net rate of reaction calculated by the BVE must be zero in a given phase (e.g., $\nabla \cdot \mathbf{i}_{io} = 0$). Therefore, as will be made clear further below, the definition of “ η ” is inherently related to the specific form of BVE.

$$\nabla \cdot \mathbf{i}_{io} = z_e \mathcal{F} \left[k_a C_R \exp\left(\alpha_a \frac{z_e \mathcal{F}}{RT} \Delta\phi\right) - k_c C_P \exp\left(-\alpha_c \frac{z_e \mathcal{F}}{RT} \Delta\phi\right) \right] \quad (2.130)$$

$$\nabla \cdot \mathbf{i}_{io} = i_0^{\nabla} \left[\exp\left(\alpha_a \frac{z_e \mathcal{F}}{RT} \eta_{act}\right) - \exp\left(-\alpha_c \frac{z_e \mathcal{F}}{RT} \eta_{act}\right) \right] \quad (2.131)$$

$$\nabla \cdot \mathbf{i}_{io} = i_*^{\nabla} \left[\frac{C_R}{C_{R,ref}} \exp\left(\alpha_a \frac{z_e \mathcal{F}}{RT} \eta\right) - \frac{C_P}{C_{P,ref}} \exp\left(-\alpha_c \frac{z_e \mathcal{F}}{RT} \eta\right) \right] \quad (2.132)$$

Where k_a and k_c are the rate constants for the anodic and cathodic reactions, respectively, and C_R and C_P are the local (TPB) concentrations of the anodic and cathodic reactants, respectively. Equations (2.131) and (2.132) are two alternative BVEs that use η_{act} and η , respectively, for the archetypal oxidation reaction (2.129). In the first equation, i_0^{∇} is the exchange current density defined at the local gas composition. Likewise in the second equation i_*^{∇} is the corresponding exchange current density defined at reference conditions. Equation (2.130) is the “primitive form” from which the two other equations can be derived.

In Eq. (2.132) $\Delta\phi_{eq}^{ref}$ is the open circuit value of $\Delta\phi$ when the concentrations of the reactant and product are $C_{R,ref}$ and $C_{P,ref}$, and i_*^{∇} is a constant representing the exchange current density at the composition $C_{R,ref}$ and $C_{P,ref}$. This reference composition might conveniently be taken to be the initial concentration of the reactant/product or the concentration prevailing external to the active layer. It does not mandatorily refer to the “bulk gas condition”. Usage of $\Delta\phi_{eq}^{ref}$ (and hence of η) is often related to situations wherein one is

dealing with potentials relative to a given reference electrode. Thus, its use is a matter of convenience. In Eq. (2.131), the exchange current density can be shown to be given by^[67]:

$$i_0^{\mathbb{V}} = z_e \mathcal{F} k_a^{\alpha_c} k_c^{\alpha_a} C_R^{\alpha_c} C_P^{\alpha_a} \quad (\text{a parameter that varies with local composition}) \quad (2.133)$$

In the derivation of Eq. (2.133), it was assumed that the cathodic and anodic reactions are first order with respect to reactants, although generalization to an arbitrary order is straightforward.

The equation above can be easily obtained if one substitutes Eq. (2.127), (2.130), and (2.134) in Eq. (2.131). In this latter equation, the local open-circuit voltage $\Delta\phi_{eq}^{tpb}$ is defined as (compare with Eq. (2.104)):

$$\Delta\phi_{eq}^{tpb} = \frac{\mathcal{RT}}{z_e \mathcal{F}} \ln \left(\frac{k_c C_P}{k_a C_R} \right) \Rightarrow \frac{z_e \mathcal{F} \Delta\phi_{eq}}{\mathcal{RT}} = \ln \left(\frac{k_c}{k_a} \right) + \ln \left(\frac{C_P}{C_R} \right) \quad (2.134)$$

In Eq. (2.132), the open-circuit voltage $\Delta\phi_{eq}^{ref}$ is defined as (compare it with Eq. (2.73), (2.74), (2.38), and (2.39)):

$$\Delta\phi_{eq}^{ref} = \frac{\mathcal{RT}}{z_e \mathcal{F}} \ln \left(\frac{k_c C_{P,ref}}{k_a C_{R,ref}} \right) \quad (2.135)$$

Substituting Eq. (2.135) in Eq. (2.132) yields for the RHS:

$$\begin{aligned} i_*^{\mathbb{V}} & \left\{ \frac{C_R}{C_{R,ref}} \exp \left[\alpha_a \frac{z_e \mathcal{F}}{\mathcal{RT}} (\Delta\phi - \Delta\phi_{eq}^{ref}) \right] - \frac{C_P}{C_{P,ref}} \exp \left[-\alpha_c \frac{z_e \mathcal{F}}{\mathcal{RT}} (\Delta\phi - \Delta\phi_{eq}^{ref}) \right] \right\} = \\ & = i_*^{\mathbb{V}} \left\{ \frac{C_R}{C_{R,ref}} \exp \left[\alpha_a \frac{z_e \mathcal{F}}{\mathcal{RT}} \left(\Delta\phi - \frac{\mathcal{RT}}{z_e \mathcal{F}} \ln \left(\frac{k_a C_{P,ref}}{k_c C_{R,ref}} \right) \right) \right] + \right. \\ & \quad \left. - \frac{C_P}{C_{P,ref}} \exp \left[-\alpha_c \frac{z_e \mathcal{F}}{\mathcal{RT}} \left(\Delta\phi - \frac{\mathcal{RT}}{z_e \mathcal{F}} \ln \left(\frac{k_c C_{P,ref}}{k_a C_{R,ref}} \right) \right) \right] \right\} \\ & = i_*^{\mathbb{V}} \left\{ \frac{C_R}{C_{R,ref}} \exp \left[\frac{\alpha_a z_e \mathcal{F}}{\mathcal{RT}} \Delta\phi \right] \exp \left[-\alpha_a \ln \left(\frac{k_c C_{P,ref}}{k_a C_{R,ref}} \right) \right] + \right. \\ & \quad \left. - \frac{C_P}{C_{P,ref}} \exp \left[-\frac{\alpha_c z_e \mathcal{F}}{\mathcal{RT}} \Delta\phi \right] \exp \left[\alpha_c \ln \left(\frac{k_c C_{P,ref}}{k_a C_{R,ref}} \right) \right] \right\} \\ & = i_*^{\mathbb{V}} \left[\frac{C_R}{C_{R,ref}} \left(\frac{k_a C_{R,ref}}{k_c C_{P,ref}} \right)^{\alpha_a} \exp \left(\frac{\alpha_a n F}{\mathcal{RT}} \Delta\phi \right) - \frac{C_P}{C_{P,ref}} \left(\frac{k_c C_{P,ref}}{k_a C_{R,ref}} \right)^{\alpha_c} \exp \left(-\frac{\alpha_c n F}{\mathcal{RT}} \Delta\phi \right) \right] \\ & = i_*^{\mathbb{V}} \left[\frac{C_R}{C_{P,ref}^{\alpha_a}} \left(\frac{k_a}{k_c} \right)^{\alpha_a} C_{R,ref}^{\alpha_a-1} \exp \left(\frac{\alpha_a z_e \mathcal{F}}{\mathcal{RT}} \Delta\phi \right) - \frac{C_P}{C_{R,ref}^{\alpha_c}} \left(\frac{k_c}{k_a} \right)^{\alpha_c} C_{P,ref}^{\alpha_c-1} \exp \left(-\frac{\alpha_c z_e \mathcal{F}}{\mathcal{RT}} \Delta\phi \right) \right] \end{aligned} \quad (2.136)$$

With the exchange current density $i_*^{\mathbb{V}}$ defined by:

$$i_*^{\mathbb{V}} = z_e \mathcal{F} C_{R,ref}^{\alpha_c} C_{P,ref}^{\alpha_a} k_a^{\alpha_c} k_c^{\alpha_a} \quad (\text{a constant parameter in } z) \quad (2.137)$$

Then,

$$\begin{aligned}
&= z_e \mathcal{F} C_{R,ref}^{\alpha_c} C_{P,ref}^{\alpha_a} k_a^{\alpha_c} k_c^{\alpha_a} \left\{ \frac{C_R}{C_{P,ref}^{\alpha_a}} \left(\frac{k_a}{k_c} \right)^{\alpha_a} C_{R,ref}^{\alpha_a-1} \exp \left[\frac{\alpha_a z_e \mathcal{F}}{RT} \Delta \phi \right] + \right. \\
&\quad \left. - \frac{C_P}{C_{R,ref}^{\alpha_c}} \left(\frac{k_c}{k_a} \right)^{\alpha_c} C_{P,ref}^{\alpha_c-1} \exp \left[-\frac{\alpha_c z_e \mathcal{F}}{RT} \Delta \phi \right] \right\} \\
&= z_e \mathcal{F} \left[C_R C_{R,ref}^{\alpha_a+\alpha_c-1} k_a^{\alpha_a+\alpha_c} \exp \left(\frac{\alpha_a z_e \mathcal{F}}{RT} \Delta \phi \right) - C_P C_{P,ref}^{\alpha_a+\alpha_c-1} k_c^{\alpha_a+\alpha_c} \exp \left(-\frac{\alpha_c z_e \mathcal{F}}{RT} \Delta \phi \right) \right]
\end{aligned} \tag{2.138}$$

If $\alpha_a + \alpha_c = 1$, one finally obtains

$$\nabla \cdot \mathbf{i}_{io} = z_e \mathcal{F} \left[C_R k_a \exp \left(\frac{\alpha_a z_e \mathcal{F}}{RT} \Delta \phi \right) - C_P k_c \exp \left(-\frac{\alpha_c z_e \mathcal{F}}{RT} \Delta \phi \right) \right] \tag{2.139}$$

Which is exactly the “primitive form” of the BVE, *c.f.*, Eq.(2.130). Thus, one sees that both Eq. (2.131) and (2.132) are equivalent, despite their differences in form (in respect to “ η_{act} ” or “ η ”).

In Kulikovsky’s model (see §§4.3.2), the following equation states that Ohm’s law should be valid for the electrolyte phase, relating the ionic current to the overvoltage gradient:

$$i_{io} = -\sigma_{io} \frac{\partial \eta(z)}{\partial z} \tag{2.140}$$

In the case where $\eta = \eta_{act}$ in (2.140), Kulikovsky’s model does not hold unless:

- i. If one neglects the ohmic losses in the electronic phase and thus if it is assumed that the phase potential ϕ_{elde} is a constant (see §§2.3.2 and §§2.3.3).
- ii. And if $\Delta \phi_{eq}$ is also assumed constant (it has already been seen that, rigorously speaking, this potential difference varies along the thickness of the active layer if the chemical activity of reacting species is allowed to vary).

That is, from Eq. (2.88), (2.92), (2.93), and (2.127)

$$\frac{\partial \eta_{act}}{\partial z} = \frac{\partial (\phi_{elde} - \phi_{elyt} - \Delta \phi_{eq})}{\partial z} = -\frac{\partial \phi_{elyt}}{\partial z} = \frac{i_{io}}{\sigma_{io}} \Leftrightarrow \frac{\partial \phi_{elde}}{\partial z} = 0 \text{ and } \frac{\partial \phi_{eq}}{\partial z} = 0 \tag{2.141}$$

It is true that if the gas composition varies along the thickness of the active layer, $\Delta \phi_{eq}$ will also change, invalidating the physical pertinence of Eq.(2.140), in the case where $\eta = \eta_{act}$. Furthermore, we note that in Eq. (2.140) η is switched in sign in comparison to Eq. (2.141). This is because the sign of the current flux (which is oriented the opposite way to the electron flux) must be physically consistent with the adopted reference frame (*e.g.*, orientation of coordinate axes). For example, in the anodic half-cell the current vector is directed from the anode outer layer toward the electrolyte. If this vector is not pointing in the positive direction of the coordinate axis, the current density (electronic and ionic) will be negative-valued. As a matter of convenience, it appears that Kulikovsky chose to consider only positive values for both polarization and current densities, irrespective of which half-cell (anodic or cathodic) is modeled.

To put it concisely, it is not clear whether “ η ” refers to the activation polarization, Eq.(2.127), or to the total polarization, Eq. (2.128), in Kulikovsky model. More likely it is the latter situation, that is, Kulikovsky is modeling the “augmented polarization” and not the activation polarization profiles. Only in the case of ideal gas-phase transport is when “ η ” reduces to “ η_{act} ”. Moreover, If “ η ” is the augmented polarization then Eq. (2.123) is not rigorously correct because, as has already been pointed out previously, the reactant concentration multiplies both the forward and reverse reaction rates. This suggests, in principle, that the feed reactant would have the same stoichiometric coefficient in both sides of the chemical reaction equation. In other words, one arrives at the paradoxical conclusion that in this case the feed gas is neither a reactant nor a product! Nonetheless, the value i_*^V still follows the expected physics in that the exchange current density increases if either the reactant or product concentration is increased (see Eq. (2.126) and (2.137)). That is, an increase of either reactant or product concentration should shift the equilibrium potential such that both the forward and reverse reaction rates remain equal.

By way of example, if η_{act} was to be used in place of η , then one should reformulate the system of equations (2.123) and (2.140) as:

$$\frac{\partial i_{io}}{\partial z} = -2 i_0^V \sinh(\eta_{act}/b_{ts}) \quad (2.142)$$

$$i_{io} = \sigma_{io} \left(\frac{\partial \eta_{act}}{\partial z} + \frac{\partial \Delta \phi_{eq}}{\partial z} \right) \quad (2.143)$$

Where $\Delta \phi_{eq} = \Delta \phi_{eq}(C_{fg})$, according to Eq. (2.64) or (2.65).

A final remark, but not an unimportant one, concerns the distinctiveness between local, augmented, and integral values of polarization, so that we are sure about what one is exactly referring to. Starting with Eq. (2.127) and differentiating it with respect to z :

$$\frac{\partial \eta_{act}}{\partial z} = \frac{\partial \phi_{elde}}{\partial z} - \frac{\partial \phi_{elyt}}{\partial z} - \frac{\partial (\Delta \phi_{eq}^{tpb})}{\partial z} \quad (2.144)$$

Then,

$$\begin{aligned} \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial \eta_{act}}{\partial z} \right) dz &= \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial \phi_{elde}}{\partial z} \right) dz - \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial \phi_{elyt}}{\partial z} \right) dz - \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial (\Delta \phi_{eq}^{tpb})}{\partial z} \right) dz \\ \eta_{act}(z_0 + \Delta z) &= \eta_{act}(z_0) + [\phi_{elde}(z_0 + \Delta z) - \phi_{elde}(z_0)] + \\ &\quad - [\phi_{elyt}(z_0 + \Delta z) - \phi_{elyt}(z_0)] - [\Delta \phi_{eq}^{tpb}(z_0 + \Delta z) - \Delta \phi_{eq}^{tpb}(z_0)] \\ \eta_{act}(z_0 + \Delta z) &= \eta_{act}(z_0) - \eta_{ohm,e}^{\Delta z} + \eta_{ohm,io}^{\Delta z} - \eta_{conc}^{\Delta z} \\ \Rightarrow \Delta \eta_{act}(z_0, \Delta z) &= \eta_{ohm,io}^{\Delta z} - \eta_{ohm,e}^{\Delta z} - \eta_{conc}^{\Delta z} \end{aligned} \quad (2.145)$$

Where $\eta_{ohm}^{\Delta z}$ is the potential difference that would be measured with no concentration gradients, within the thin segment $z_0 + \Delta z$ of the active layer thickness; similarly, $\eta_{conc}^{\Delta z}$ is the potential changes induced by concentration effects within the thin segment $z_0 + \Delta z$. If we neglect the ohmic losses associated with the electronic phase, then

$$\Delta\eta_{act}(z_0, \Delta z) = \eta_{ohm,io}^{\Delta z} - \eta_{conc}^{\Delta z} \quad (2.146)$$

Considering the overall thickness of the active-layer, one has

$$\eta_{act}^{total} = \Delta\eta_{act}(0, l_t) = \eta_{ohm,io} - \eta_{conc} \quad (2.147)$$

Considering the case of ideal gas-phase transport

$$\eta_{act}^{total} = \Delta\eta_{act}(0, l_t) = \eta_{ohm,io} \quad (2.148)$$

Where the ohmic voltage drop in the electrolyte phase may be calculated as:

$$\eta_{ohm,io}^{\Delta z} = \int_{z_0}^{z_0+\Delta z} \frac{i_{io} dz}{\sigma_{io}} \quad \text{or in nondimensional form,} \quad \hat{\eta}_{ohm,io}^{\Delta z} = \int_{\hat{z}_0}^{\hat{z}_0+\Delta\hat{z}} \hat{i}_{io} d\hat{z} \quad (2.149)$$

If one now considers Eq. (2.128) instead, then

$$\int_{z_0}^{z_0+\Delta z} \left(\frac{\partial \eta}{\partial z} \right) dz = \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial \phi_{elde}}{\partial z} \right) dz - \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial \phi_{elyt}}{\partial z} \right) dz - \int_{z_0}^{z_0+\Delta z} \left(\frac{\partial (\Delta \phi_{eq}^{ref})}{\partial z} \right) dz = 0 \quad (2.150)$$

$$\Rightarrow \Delta\eta(z_0, \Delta z) = \eta_{ohm,io}^{\Delta z} - \eta_{ohm,e}^{\Delta z}$$

And thus,

$$\Delta\eta(z_0, \Delta z) = \Delta\eta_{act}(z_0, \Delta z) + \Delta\eta_{conc}(z_0, \Delta z) = \eta_{ohm,io}^{\Delta z} - \eta_{ohm,e}^{\Delta z} \quad (2.151)$$

If one neglects the ohmic losses associated with the electronic phase, then

$$\Delta\eta(z_0, \Delta z) = \Delta\eta_{act}(z_0, \Delta z) + \Delta\eta_{conc}(z_0, \Delta z) = \eta_{ohm,io}^{\Delta z} \quad (2.152)$$

What is interesting about Eq. (2.145)-(2.152) is that these equations portray the cell polarization from the perspective of the “ohmic expenditure” in the ionic phase of a composite electrode. In this fashion, although the electrode overvoltage η does not represent a physical electric potential difference (see **§§2.3.1**), it can conveniently be represented by the ohmic loss contributions of the different components of electrode. Another interesting result is the negative sign in front of the term associated with electronic ohmic losses in Eq. (2.145) and (2.150). It suggests that by decreasing the electronic conductivity in comparison to the ionic conductivity, the average electrochemical reaction rate (e.g., $1/l_t \int \nabla \cdot \mathbf{i}_{io} dz$) will increase accordingly. However, this will also smooth out the reaction rate profile along the electrode thickness (see figures 2.12 and 2.13), fact that might require a thicker active layer, thereby increasing the

overall ohmic loss. Thus, once more, one verifies the existing compromise between ohmic losses and reaction rates, as discussed in **§§2.3.3**.

In one of his models (see **APPENDIX A**) concerning the case of ideal ionic transport¹¹, Kulikovsky^[12, 107] has made the inconsistent assumption of a vanishing small overvoltage gradient ($\nabla\eta \rightarrow 0$), based on the use of an augmented polarization setup. From Eq. (2.151) one finds that the augmented polarization η is also function of the concentration polarization η_{conc} and for that it is not possible to readily assume that $\eta \cong \eta_0, \forall z$. The concentration polarization can attain sufficient importance to such extent that the overvoltage gradient will vary along the active layer thickness. As a result of this undue assumption, the model developed by Kulikovsky in **§§A.2** is restricted to only low current density values, where concentration polarization processes are not expected to occur in an important manner. That is, by assuming $\nabla\eta \rightarrow 0$ the author also (unduly) restricts the concentration polarization to relatively small values ($\eta_{conc} \rightarrow 0$).

¹¹ Thus a case wherein mass transport limitations in the gas-phase are taken into consideration (and thus so are concentration polarizations) and the ionic transport is, on the other hand, disregarded completely.

Chapter 3

MASS TRANSFER LIMITATIONS AND CONCENTRATION LOSSES

3.1 Introduction

Under real operating conditions, SOFC chemical and electrochemical reactions can only proceed at a limited rate. Moreover, the empirical situation is that, with a few exceptions involving extraordinary (idealized) conditions, reactions will proceed slowly. The rate at which these reactions can occur will depend on the interplay of multiscale physicochemical processes, which all together are deeply influenced by the micromorphology details of SOFC functional layers. Thus, a practical issue of central importance is to identify and describe, intelligibly, what limits SOFC reaction rates. This surely is, and has been, an enormous scientific challenge^[6, 7, 13, 8].

As described in §§1.3.2, to generate electricity, the SOFC must be continuously supplied with fuel and oxidant to avoid fuel cell “starvation”. Concurrently, products must be continuously removed as to avoid “strangling” the SOFC. This overall process of supplying reactants and removing products is what constitutes the seeming, macroscopic essence of fuel cell mass transport¹. As it will be discussed in more detail, poor mass transfer can lead to substantial performance loss, which is often termed as “concentration-induced losses” of a SOFC electrode. This loss is, ultimately, the result of some adverse density distribution of reactants and products over the active area of electrocatalysts. The gas-phase chemical potential gradient provides one of the main, but not the only, “thermodynamic forces” driving the diffusive transport of reactants and products, to and from the reaction zones, respectively. This spatial difference in chemical potential develops, to a great extent, as the result of

¹ The focus of this work is on gas-phase phenomena. However, there is also the solid-phase ionic transport of oxygen ions (in the electrolyte and also in ionic conducting phases of composite electrodes). Ionic transport is actually a subset of mass transport where the mass being transported consists of charged ions^[87, 88, 89].

heterogeneous reactions (species consumption/production) occurring within the buffer-layer and electrode active layers (see figures 1.15 and 3.1). Thus, one can perceive a delicate and yet dynamic balance between material fluxes and driving forces that might lead to reactant depletion, or product accumulation, in the reaction zones, affecting the SOFC performance. Furthermore, as there is a strong interdependence between mass transport and surface-catalyzed reactions, which involves the active (transition-metal) catalyst, one should also take into consideration the feedback of chemical reactions in response to the local (spatial varying) properties of the catalytic substrate, along the interface between the pore-wall and fluid-layer.

Figure 3.1: SOFC cross-section illustrating the overall steps related to mass transfer and interdependent processes: (1) reactant delivery (transport) into the SOFC; (2) fuel reforming reactions; (3) electrochemical reactions; (4) ionic or electronic conduction (charge transport); (5) removal of product and/or reactant excess from SOFC (figure by the author).

The definition of concentration polarization, as ordinarily found in the literature, was given in §2.2.2 and expressed by Eq. (2.37) and (2.38) for the anode and cathode, respectively. Now, that definition should be expanded through the incorporation of complementary concepts. First and foremost, it will be pointed out that “mass transport loss” should not to be (always) taken as equivalent of “concentration polarization”. SOFC mass transport losses encompass more than the sole effect of chemical potential gradients in gas-phase. These losses can reflect the combination of direct and indirect (cross) effects arising from competing transport phenomena, especially those cross-effects between individual irreversible processes, whose impact usually lessens the velocity of electrochemical reactions and that is rarely obvious under a superficial examination of the problem. The discussion to follow is restricted to the domain of steady state processes. The analysis of models with respect to their shortcomings, misconceptions, and inaccuracies is not pursued at this point, a task which is fulfilled in the next chapter wherein chosen models are critically reviewed.

3.2 Preliminaries on Concentration Polarization

When electroactive chemical species (*i.e.*, species that directly participate in the course of electrochemical reactions) are present at different concentrations (activities), a voltage difference develops^[67]. This voltage “build-up” portrays the fact that electrochemical potentials are offsetting one another to maintain the thermodynamic equilibrium (*i.e.*, zero net reaction rate and balanced electric charges at electroactive sites). More precisely, equilibrium is established when an electrical potential gradient builds up sufficiently to exactly counterbalance the chemical potential gradient:

$$\left(\sum_i v_i \tilde{\mu}_i \right)_{\text{products}} - \left(\sum_j v_j \tilde{\mu}_j \right)_{\text{reactants}} = 0 \quad (3.1)$$

From which Eq. (2.43) was previously derived, also using the definition of electrochemical potential, Eq. (2.42). As mentioned in **§§2.3.1**, $\Delta\phi_i$ represents the “built-up electrical potential” for the charges that are moved on the reaction sites, per-mole basis of a given reactant. Thus, one could say that the chemical potential difference between the bulk gas and the gas effectively contacting electrochemical reaction sites forms a concentration cell^[109], whose cell voltage would oppose the overall SOFC’s EMF and which may be seen as a voltage loss (polarization). From Eq. (2.43) follows that (see **§§3.3.1** for the exact expressions on cathode and anode sides):

$$\Delta\phi_{elde}^{bulk} - \Delta\phi_{elde}^{tpb} = -\frac{RT}{\Delta z_e \mathcal{F}} \ln \left(\frac{\prod_i a_{product,i}^{v_i}}{\prod_j a_{reactant,j}^{v_j}} \right)_{bulk} + \frac{RT}{\Delta z_e \mathcal{F}} \ln \left(\frac{\prod_i a_{product,i}^{v_i}}{\prod_j a_{reactant,j}^{v_j}} \right)_{tpb} \quad (3.2)$$

$$\Delta\phi_{elde}^{bulk} - \Delta\phi_{elde}^{tpb} = \frac{RT}{\Delta z_e \mathcal{F}} \ln \left(\frac{\prod_j a_{reactant,j,bulk}^{v_j}}{\prod_j a_{reactant,j,tpb}^{v_j}} \frac{\prod_i a_{product,i,tpb}^{v_i}}{\prod_i a_{product,i,bulk}^{v_i}} \right), \quad \text{where } \Delta z_e \text{ may be either positive or negative.}$$

$$\eta_{conc} = E_{rev}^{bulk} - E_{rev}^{tpb} = -(\Delta\phi_{elde}^{bulk} - \Delta\phi_{elde}^{tpb}) \quad (3.3)$$

The application of these expressions only makes sense if the reversible voltage (E_{rev}) is evaluated by taking a certain reference for the concentration of electroactive species, in this case the bulk gas concentration (E_{rev}^{bulk}). The concentration polarization η_{conc} , which is discounted from E_{rev}^{bulk} , may be seen as the “voltage surplus” that would be available if the concentration of electroactive species at the TPB was the same as that in the bulk flow. The polarization defined by Eq. (3.3) is also known as Nernstian loss, because the effects of gas concentration on reversible cell voltage are modeled by the Nernst equation. Considering the case of a hydrogen/oxygen SOFC, Eq. (3.2) can be shown to give Eq. (2.37) and (2.38), as will be seen in **§§3.3.1**.

Without delving into the intricate details of convective and diffusive “forces”, which are often interwoven with other driving forces, the intent here is to first establish a conceptual interpretation for the relation between reactants and products transport, and the concentration polarization (η_{conc}). Therefore, it will be of no relevance in what follows to bring forth a discussion about “everything” that might affect such transport. At this point, it is assumed that transport is essentially diffusive and that electrochemical reactions are solely responsible for driving the diffusion of gas-phase species.

In the example of a hydrogen/oxygen fuel cell (see Fig. 3.2), the depletion of H_2 in the vicinity of the TPB extends out into the anode, because the diffusive transport of H_2 , from the bulk flow to the reaction zones, has a finite rate. In this example, therefore, the concentration gradient constitutes the essential driving force for the mass transport process through this electrode. The concentration of H_2 in the gas phase falls from its bulk value ($C_{H_2,bulk}$) at the flow channel to a lower value ($C_{H_2,an/elyt}$) at the anode/electrolyte interface. Here it is assumed to be possible to define a stagnant gas region (“diffusion layer”) with diffusion-dominated transport. Although the delimitation of such region is unrealistic or, at most, hardly defined, it introduces an important characterization parameter: the diffusion layer thickness (δ_{diff}).

Figure 3.2: simplified mass transport problem in the anode of a SOFC. A perfect mixing of reactants and products in the bulk flow (gas channel) is assumed, and thus an invariant bulk concentration ($C_{H_2,bulk}$ and $C_{H_2O,bulk}$). Electroactive species are consumed/generated within the active layer, potentially leading to reactant depletion or/and product accumulation. As a result, concentration gradients are established along the diffusion layer (figure by the author).

This thickness serves to line off hypothetical “boundary lines” between convection-dominated and diffusion-dominated regions, where the gas channel and porous electrode meet at one of the boundaries. The diffusion layer thickness, being itself an abstraction, does not coincide, necessarily, with the electrode thickness. In other words, the diffusion layer thickness should be taken as a pseudo-geometric parameter. In the oversimplified situation depicted in Fig. 3.2, the reactant depletion (or product accumulation) can affect SOFC performance through the combination of two “loss effects”, namely “Nernstian losses” and “concentration-induced kinetic losses”. The collective effect of these losses is what the literature generally refers to as the SOFC mass transport losses. As already advised in the preceding paragraphs, the mass transport loss reveals itself far more complex than this prevailing view wherein the loss is only associated with the difference between TPB and bulk concentrations of reactants and products (see §§3.6).

3.3 Thermostatics of Concentration Polarization

3.3.1 Concentration Cell and “Virtual Balance” of Electrochemical Potentials

The electric potential difference ($\Delta\phi$) of the “virtual” concentration cell that forms on the anode or cathode can be evaluated by assuming that the respective electrochemical potentials, at either “bulk conditions” or “three-phase-boundary conditions”, are offsetting one another to maintain the thermodynamic equilibrium. Applying Eq. (2.42) and (2.43) for reaction (2.44), at both “bulk gas” and TPB conditions, then

$$\mu_{H_2O}^{\hat{}} + \mathcal{R}T \ln a_{H_2O,bulk} + \mu_{V_O}^{\hat{}} + 2\mu_{e'}^{\hat{}} - 2\mathcal{F} \phi_{e'}^{bulk} - \left[\mu_{H_2}^{\hat{}} + \mu_{O_2}^{\hat{}} + \mathcal{R}T \left(\ln a_{H_2,bulk} + \ln a_{O_2,bulk} \right) - 2\mathcal{F} \phi_{O_2}^{bulk} \right] = 0 \quad (3.4)$$

$$\mu_{H_2O}^{\hat{}} + \mathcal{R}T \ln a_{H_2O,tpb} + \mu_{V_O}^{\hat{}} + 2\mu_{e'}^{\hat{}} - 2\mathcal{F} \phi_{e'}^{tpb} - \left[\mu_{H_2}^{\hat{}} + \mu_{O_2}^{\hat{}} + \mathcal{R}T \left(\ln a_{H_2,tpb} + \ln a_{O_2,tpb} \right) - 2\mathcal{F} \phi_{O_2}^{tpb} \right] = 0 \quad (3.5)$$

Subtracting Eq. (3.5) from Eq. (3.4), and assuming that $\Delta a_{O_2}^{\hat{}} = 0$, it yields

$$\begin{aligned} \mathcal{R}T \left(\ln a_{H_2O,bulk} - \ln a_{H_2O,tpb} + \ln a_{H_2,tpb} - \ln a_{H_2,bulk} \right) - 2\mathcal{F} \left(\phi_{e'}^{bulk} - \phi_{e'}^{tpb} \right) &= 0 \\ \phi_{e'}^{bulk} - \phi_{e'}^{tpb} - \left(\phi_{O_2}^{bulk} - \phi_{O_2}^{tpb} \right) &= \Delta\phi_{e'} - \Delta\phi_{O_2}^{\hat{}} = \Delta\phi_{an}^{bulk} - \Delta\phi_{an}^{tpb} = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{H_2O,bulk} a_{H_2,tpb}}{a_{H_2,bulk} a_{H_2O,tpb}} \right) \end{aligned} \quad (3.6)$$

Finally, one can define:

$$\eta_{C,an} \equiv E_{rev}^{bulk} - E_{rev}^{tpb} = -(\phi_{an}^{bulk} - \Delta\phi_{an}^{tpb}) = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{H_2,bulk} a_{H_2O,tpb}}{a_{H_2O,bulk} a_{H_2,tpb}} \right) \quad (3.7)$$

$$\Rightarrow \eta_{C,an} \geq 0 \quad (a_{H_2,bulk}/a_{H_2,tpb} \geq 1 \text{ and } a_{H_2O,tpb}/a_{H_2O,bulk} \geq 1) \quad (3.8)$$

In Eq. (3.6) it was assumed that both the activity ($a_{O_o^\times}$) of oxide ions, on/near the solid electrolyte surface, are not affected by the chemical activity of adjacent gas-phase species, that is, $a_{O_o^\times,bulk} \approx a_{O_o^\times,tpb}$. The activity of conducting electrons in metals is assumed to be “1”, as is the activity of pure components, hence these terms vanish from the equations. In Eq. (3.7), it was also used the result of Eq. (2.61). The development for the cathode of an SOFC has an analogous procedure, but considers the reaction given by (2.46) instead:

$$\mu_{O_o^\times}^\dagger + \mathcal{R}T \ln a_{O_o^\times,bulk} - 2\mathcal{F} \phi_{O_o^\times}^{bulk} - \left(\frac{1}{2} \mu_{O_2}^\dagger + \frac{1}{2} \mathcal{R}T \ln a_{O_2,bulk} + \mu_{V_o^\bullet}^\dagger + 2\mu_{e'}^\dagger - 2\mathcal{F} \phi_{e'}^{bulk} \right) = 0 \quad (3.9)$$

$$\mu_{O_o^\times}^\dagger + \mathcal{R}T \ln a_{O_o^\times,tpb} - 2\mathcal{F} \phi_{O_o^\times}^{tpb} - \left(\frac{1}{2} \mu_{O_2}^\dagger + \frac{1}{2} \mathcal{R}T \ln a_{O_2,tpb} + \mu_{V_o^\bullet}^\dagger + 2\mu_{e'}^\dagger - 2\mathcal{F} \phi_{e'}^{tpb} \right) = 0 \quad (3.10)$$

Subtracting Eq. (3.10) from Eq. (3.9) and assuming that $\Delta a_{O_o^\times} = 0$, it yields

$$\begin{aligned} \frac{1}{2} \mathcal{R}T (\ln a_{O_2,tpb} - \ln a_{O_2,bulk}) + 2\mathcal{F} (\phi_{e'}^{bulk} - \phi_{e'}^{tpb}) - 2\mathcal{F} (\phi_{O_o^\times}^{bulk} - \phi_{O_o^\times}^{tpb}) &= 0 \\ (\phi_{e'}^{bulk} - \phi_{e'}^{tpb}) - (\phi_{O_o^\times}^{bulk} - \phi_{O_o^\times}^{tpb}) &= \Delta \phi_{e'} - \Delta \phi_{O_o^\times} = \Delta \phi_{ca}^{bulk} - \Delta \phi_{ca}^{tpb} = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{\sqrt{a_{O_2,bulk}}}{\sqrt{a_{O_2,tpb}}} \right) \end{aligned} \quad (3.11)$$

Finally, one can define:

$$\eta_{C,ca} \equiv E_{rev}^{bulk} - E_{rev}^{tpb} = -(\phi_{ca}^{bulk} - \Delta \phi_{ca}^{tpb}) = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{\sqrt{a_{O_2,tpb}}}{\sqrt{a_{O_2,bulk}}} \right) = \frac{\mathcal{R}T}{4\mathcal{F}} \ln \left(\frac{a_{O_2,tpb}}{a_{O_2,bulk}} \right) \quad (3.12)$$

$$\Rightarrow \eta_{C,ca} < 0 \quad (a_{O_2,tpb}/a_{O_2,bulk} \geq 1) \quad (3.13)$$

Note that the sign (*i.e.*, polarity) of Eq. (3.8) and (3.13) depends on the direction of the electrochemical reactions considered (Eq. (2.44) and (2.46), respectively). Thus, the sign associated with electric potentials (and polarizations) is not completely arbitrary. Attention is much needed in setting up the calculation of electromotive “forces” and electric potential differences (see §§2.3.1), so that thermodynamic consistency is not compromised. *Ad hoc* absolute values are widely applied in the literature to “work around” this issue.

In respect to the cathode, Eq. (3.9) and (3.10) indicate that the concentration polarization could either increase or decrease, depending on whether the activity of oxide ions is affected by the activity of O_2 near the gas/solid interface, according to Eq. (3.14):

$$\eta_{C,ca}^* = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{\sqrt{a_{O_2,tpb}}}{\sqrt{a_{O_2,bulk}}} \frac{a_{O_o^\times,bulk}}{a_{O_o^\times,tpb}} \right) = \eta_{C,ca} + \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{O_o^\times,bulk}}{a_{O_o^\times,tpb}} \right) \quad (3.14)$$

The assumption $a_{O_2}^{bulk} \approx a_{O_2}^{tpb}$ was initially enforced to make possible the derivations above. To verify this, one needs to know how the differences of potential step and activity relate to changes in the contact chemistry and space charge zone near the interface^[87, 110, 111]. Now, when analyzing both concentration polarizations in conjunction (anodic plus cathodic contribution), using their full definitions (without neglecting oxide-ion related terms), it yields

$$\begin{aligned} \eta_{C,an} + |\eta_{C,ca}| &= \frac{RT}{2\mathcal{F}} \left[\ln \left(\frac{a_{H_2,bulk} a_{H_2O,tpb} \sqrt{a_{O_2,bulk}}}{a_{H_2O,bulk} a_{H_2,tpb} \sqrt{a_{O_2,tpb}}} \right) + \ln \left(\frac{a_{O_2}^{bulk,an}}{a_{O_2}^{tpb,an}} \right) + \ln \left(\frac{a_{O_2}^{tpb,ca}}{a_{O_2}^{bulk,ca}} \right) \right] \\ &= E_{rev}^{buk} - E_{rev}^{tpb} + \frac{RT}{2\mathcal{F}} \left[\ln \left(\frac{a_{O_2}^{tpb,ca}}{a_{O_2}^{tpb,an}} \right) - \ln \left(\frac{a_{O_2}^{bulk,ca}}{a_{O_2}^{bulk,an}} \right) \right] = E_{rev}^{buk} - E_{rev}^{tpb} + \frac{RT}{2\mathcal{F}} \Delta \left(\frac{a_{O_2}^{ca}}{a_{O_2}^{an}} \right) \end{aligned} \quad (3.15)$$

Where the definition of the LHS of concentration polarizations should include all pertinent electric potential differences:

$$\begin{aligned} \eta_{C,an} + |\eta_{C,ca}| &= -[\Delta\phi_{e'} - \Delta\phi_{O_2}^*]_{an} - [\Delta\phi_{O_2}^* - \Delta\phi_{e'}]_{ca} \\ &= \Delta\phi_{e',ca} - \Delta\phi_{e',an} + \Delta\phi_{O_2}^{*,an} - \Delta\phi_{O_2}^{*,ca} \end{aligned} \quad (3.16)$$

In Eq. (3.15), when in thermodynamic equilibrium (*i.e.*, zero net current density), each of the last two terms in square brackets must vanish and $E_{rev}^{buk} = E_{rev}^{tpb}$. However, for finite values of current density this is not necessarily true (see comments at the end of §2.3.1). Nevertheless, one might argue that the overall contribution of these last two terms, *i.e.* $\Delta(a_{O_2}^{ca}/a_{O_2}^{an})$, should be very small even under non-equilibrium conditions if the ratio $a_{O_2}^{ca}/a_{O_2}^{an}$ is approximately linear with respect to current density, albeit the possibility of anodic and cathodic oxide-ions contributions not being negligible if evaluated separately, as in the cathodic case of Eq. (3.14).

For simplicity, one can show that when the electric potential variation in the ionic phase ($\Delta\phi_{O_2}^*$) is approximately equal to the ohmic voltage loss (η_{ohm}), the respective variation of chemical activity ($a_{O_2}^*$) is approximately zero. In order to do so, one starts with the Nernst-Einstein equation^[87, 88, 69]:

$$\begin{aligned} \nabla_z \cdot i_{io} &= \frac{\partial}{\partial z} \left(-\frac{\sigma_{io}}{2\mathcal{F}} \frac{\partial \tilde{\mu}_{O_2}^*}{\partial z} \right) \Leftrightarrow \int \nabla_z \cdot i_{io} dz = \int \frac{\partial}{\partial z} \left(-\frac{\sigma_{io}}{2\mathcal{F}} \frac{\partial \tilde{\mu}_{O_2}^*}{\partial z} \right) dz \\ \Rightarrow i_{io} &= -\frac{\sigma_{io}}{2\mathcal{F}} \frac{\partial \tilde{\mu}_{O_2}^*}{\partial z} \Leftrightarrow 2\mathcal{F} \int \frac{i_{io}}{\sigma_{io}} dz = - \int \left(\frac{\partial \tilde{\mu}_{O_2}^*}{\partial z} \right) dz \\ \Rightarrow \tilde{\mu}_{O_2}^*(z) - \tilde{\mu}_{O_2}^*(z = \delta_{elde}) &= -2\mathcal{F} \int_{\delta_{elde}}^z \frac{i_{io}}{\sigma_{io}} dz \Rightarrow \tilde{\mu}_{O_2}^*(z) = \tilde{\mu}_{O_2}^{*,bulk} - 2\mathcal{F} \int_{\delta_{elde}}^z \frac{i_{io}}{\sigma_{io}} dz \\ \Rightarrow \tilde{\mu}_{O_2}^*(z = 0) &= \tilde{\mu}_{O_2}^{*,tpb} \cong \tilde{\mu}_{O_2}^{*,bulk} + 2\mathcal{F} \int_0^{\delta_{elde}} \frac{i_{io}}{\sigma_{io}} dz \end{aligned} \quad (3.17)$$

Using the definition of electrochemical potential, Eq. (2.42),

$$\tilde{\mu}_{O_2^\times} = \mu_{O_2^\times}^\circ + \mathcal{R}T \ln(a_{O_2^\times}) - 2\mathcal{F}\phi_{O_2^\times} \Rightarrow \mathcal{R}T \ln(a_{O_2^\times}) = \tilde{\mu}_{O_2^\times} - \mu_{O_2^\times}^\circ + 2\mathcal{F}\phi_{O_2^\times} \quad (3.18)$$

In Eq. (3.17), it follows that

$$\mathcal{R}T \ln\left(\frac{a_{O_2^\times,tpb,ca}}{a_{O_2^\times,bulk,ca}}\right) = \tilde{\mu}_{O_2^\times,tpb,ca} - \mu_{O_2^\times}^\circ + 2\mathcal{F}\phi_{O_2^\times,tpb,ca} - (\tilde{\mu}_{O_2^\times,bulk,ca} - \mu_{O_2^\times}^\circ + 2\mathcal{F}\phi_{O_2^\times,bulk,ca}) \quad (3.19)$$

At cathode side, and

$$\mathcal{R}T \ln\left(\frac{a_{O_2^\times,tpb,an}}{a_{O_2^\times,bulk,an}}\right) = \tilde{\mu}_{O_2^\times,tpb,an} - \mu_{O_2^\times}^\circ + 2\mathcal{F}\phi_{O_2^\times,tpb,an} - (\tilde{\mu}_{O_2^\times,bulk,an} - \mu_{O_2^\times}^\circ + 2\mathcal{F}\phi_{O_2^\times,bulk,an}) \quad (3.20)$$

At anode side. Thus, in this case one has that

$$\begin{aligned} \Delta\left(\frac{a_{O_2^\times,ca}}{a_{O_2^\times,an}}\right) &= \frac{\mathcal{R}T}{2\mathcal{F}} \left[\ln\left(\frac{a_{O_2^\times,tpb,ca}}{a_{O_2^\times,bulk,ca}}\right) - \ln\left(\frac{a_{O_2^\times,tpb,an}}{a_{O_2^\times,bulk,an}}\right) \right] = \\ &= \frac{1}{2\mathcal{F}} [\tilde{\mu}_{O_2^\times,tpb,ca} - \tilde{\mu}_{O_2^\times,bulk,ca} + 2\mathcal{F}(\phi_{O_2^\times,tpb,ca} - \phi_{O_2^\times,bulk,ca})] + \\ &\quad - \frac{1}{2\mathcal{F}} [\tilde{\mu}_{O_2^\times,tpb,an} - \tilde{\mu}_{O_2^\times,bulk,an} + 2\mathcal{F}(\phi_{O_2^\times,tpb,an} - \phi_{O_2^\times,bulk,an})] \\ &= \frac{1}{2\mathcal{F}} [\tilde{\mu}_{O_2^\times,tpb,ca} - \tilde{\mu}_{O_2^\times,bulk,ca} + \tilde{\mu}_{O_2^\times,bulk,an} - \tilde{\mu}_{O_2^\times,tpb,an} + 2\mathcal{F}(\Delta\phi_{O_2^\times,an} - \Delta\phi_{O_2^\times,ca})] \\ &= \frac{1}{2\mathcal{F}} \left[2\mathcal{F} \int_0^{\delta_{ca}} \frac{i_{io,ca}}{\sigma_{io,ca}} dz - 2\mathcal{F} \int_0^{\delta_{an}} \frac{i_{io,an}}{\sigma_{io,an}} dz + 2\mathcal{F}(\Delta\phi_{O_2^\times,an} - \Delta\phi_{O_2^\times,ca}) \right] \\ &= \int_0^{\delta_{an}} \frac{i_{io,ca}}{\sigma_{io,ca}} dz - \int_0^{\delta_{an}} \frac{i_{io,an}}{\sigma_{io,an}} dz - (\phi_{O_2^\times,bulk,ca} - \phi_{O_2^\times,tpb,ca}) + (\phi_{O_2^\times,bulk,an} - \phi_{O_2^\times,tpb,an}) \\ &= -\eta_{ohm,io,ca} - \eta_{ohm,io,an} + \Delta\phi_{O_2^\times,an} - \Delta\phi_{O_2^\times,ca} \\ &\cong -\eta_{ohm,io,ca} - \eta_{ohm,io,an} + \eta_{ohm,io,an} + \eta_{ohm,io,ca} = 0 \\ \Delta\left(\frac{a_{O_2^\times,ca}}{a_{O_2^\times,an}}\right) &= 0 \\ \therefore \ln\left(\frac{a_{O_2^\times,tpb,ca}}{a_{O_2^\times,tpb,an}}\right) &= \ln\left(\frac{a_{O_2^\times,bulk,ca}}{a_{O_2^\times,bulk,an}}\right) = \ln\left(\frac{a_{O_2^\times,bulk,an}}{a_{O_2^\times,tpb,an}}\right) = \ln\left(\frac{a_{O_2^\times,tpb,ca}}{a_{O_2^\times,bulk,ca}}\right) = 0 \end{aligned} \quad (3.21)$$

Therefore, from Eq. (3.15)-(3.21),

$$\eta_{C,an} + |\eta_{C,ca}| = E_{rev}^{buk} - E_{rev}^{tpb} = \frac{\mathcal{R}T}{2\mathcal{F}} \ln\left(\frac{a_{H_2,bulk} a_{H_2O,tpb} \sqrt{a_{O_2,bulk}}}{a_{H_2O,bulk} a_{H_2,tpb} \sqrt{a_{O_2,tpb}}}\right) \quad (3.22)$$

And both Eq. (3.7) and (3.12) are equally verified in a more general case. Thus, one finds that the chemical activity of (bulk interstitial) oxide-ions does not influence the value of concentration polarization (more precisely, the value of Nernstian polarization) at the limit when the electric potential difference within the phases is due only to ohmic effects.

3.3.2 Possible Effects of Surface Ad-ions on Concentration Polarization

In certain situations common to SOFC operation at steady state, the dependence of $a_{O_{2,ca}}^{\times}$ on the oxygen partial pressure p_{O_2} becomes relatively unimportant for $p_{O_2} > 0.15 \text{ bar}$ ^[111, 75, 112, 113], even though the electrode kinetics itself (e.g., the exchange current density) is still significantly affected by p_{O_2} (see §3.5). Nevertheless, one might question what would be the indirect effect (if any) of surface ad-ions on the evaluation of concentration polarization due to changes on the oxygen partial pressure near to that surface. Here one is not interested in how to rigorously correct for interfacial and other polarization effects, neither does one consider the complicated double-layer transients taking place near the solid-solid interfaces, however. As seen in §3.3.1, a simpler description can be obtained for small to moderate current densities when electrode's bulk composition should not be affected and the stationary current density is readily given by the electric field (ohmic) term alone of the electrochemical potential. Thus, a closed definition of concentration polarization² does not seem to pose a significant problem in this case.

In the following, it is assumed for simplicity that the ionic conductivity is solely due to oxygen-ions. Moreover, it is considered a conductivity that is averaged over all oxygen-ions (both immobile and rapid defect particles^[87]). Let the following mean-field reactions describe the “overall” oxygen reduction reaction (akin to rate-limiting steps) at TPB regions:

And denoting “ $V_O(\text{surface, elyt})$ ” as “ $V_{O,s}^{\bullet\bullet}$ ”; “ $V_O(\text{interstitial, elyt})$ ” as “ $V_{O,i}^{\bullet\bullet}$ ”; “ $O_{ad}^{2-}(\text{surface, elde})$ ” as “ $O_{O,s}^{\times}$ ”; and “ $O^{2-}(\text{interstitial, elyt})$ ” as “ $O_{O,i}^{\times}$ ”, Eq. (3.23a) and (3.23b) can be rewritten as

Thus,

One may further assume the oxygen vacancy defects to be equilibrated at all times, that is, it is assumed that the rate of transport of these defects from position $r = s + \delta_{dl}$ to the neighboring

² A definition that is independent of the activity of bulk species within the solid ionic phase.

surface layer at $r = s$ (boundary core), or vice-versa, is much faster than reaction kinetics (see Fig. 3.3). Thus, in this case

$$V_{O,s}^{\bullet\bullet}(r=s) \rightleftharpoons V_{O,i}^{\bullet\bullet}(r=s+\delta_{dl}) \quad (3.26)$$

is assumed and so one has that

$$\frac{1}{2} O_2 + 2e' \rightleftharpoons O_{O,i}^{\times}(r=s+\delta_{dl}) \quad (3.27)$$

Figure 3.3: schematic representation of a grain boundary (interface) at which the symmetry of the bulk is broken due to the introduction of structural discontinuity. Near this interface region there is an electric field acting on the surrounding bulk material, which is determined by both the charges congregated at the interface and by the spatial extent of the charge redistribution layer (“space charge layer”). This figure also illustrates the bending of thermodynamic potentials for oxide ions and which define the boundary equilibrium (note that electric potentials cause $\tilde{\mu}_{O_O}^{\times}$ to bend in the space charge zone and to shift in the core in order to satisfy the condition $\tilde{\mu} = \text{const}$). In this figure, for simplicity sake, electric bulk potentials (ϕ_{∞}) are set to zero and the shape of $\phi(r)$ near the interface is suggested by the solution of the linearized Poisson–Boltzmann equation^[114, 115] (at the low potential limit). The thickness of the grain boundary is the thickness of the grain boundary core, b_{core} , in addition to the thickness of the two space charge regions, δ_{dl} . Thus it is given by $\delta_{gb} = 2\delta_{dl} + b_{core}$. (figure by The author).

Assuming that thermodynamic equilibrium is maintained throughout the charged boundary-layer and space charge zones, the following should hold at any point (see Fig. 3.3):

$$\tilde{\mu}_{O_{O,i}}^{\times} - \tilde{\mu}_{O_{O,s}}^{\times} = 0 \quad (3.28)$$

Thus,

$$\frac{a_{O_{O,s}}^{\times}(s)}{a_{O_{O,i}}^{\times}(s + \delta_{dl})} = \exp \left[-\frac{\mu_{O_{O}}^{\times}(s) - \mu_{O_{O}}^{\times}(s + \delta_{dl})}{\mathcal{R}T} \right] \exp \left[\frac{2\mathcal{F}(\phi(s) - \phi(s + \delta_{dl}))}{\mathcal{R}T} \right] \quad (3.29)$$

The parameters $\mu_{O_{O}}^{\times}(s)$ and $\mu_{O_{O}}^{\times}(s + \delta_{dl})$ may be expressed to depend on the bulk mass action constants ($K_{O_i^{2-}}$ and $K_{O_s^{2-}}$) for the reaction Eq. (3.27):

$$-\mathcal{R}T \ln K_{O_i^{2-}} = \mu_{O_{O}}^{\times}(s + \delta_{dl}) - 2\mu_{e'}^{\dagger} - \frac{1}{2}\mu_{O_2}^{\dagger} \quad (3.30)$$

The relationship for $\mu_{O_{O}}^{\times}(s)$ is analogous to Eq. (3.30), with a modified constant $K_{O_s^{2-}}$ for the incorporation in the core zone of the surface (here it is implicitly assumed that a model based on a single adsorbed layer is adequate):

$$-\mathcal{R}T \ln K_{O_s^{2-}} = \mu_{O_{O}}^{\times}(s) - 2\mu_{e'}^{\dagger} - \frac{1}{2}\mu_{O_2}^{\dagger} \quad (3.31)$$

Equation (3.29) can now be rewritten as

$$a_{O_{O,s}}^{\times} = a_{O_{O,i}}^{\times} \frac{K_{O_s^{2-}}}{K_{O_i^{2-}}} \exp \left[\frac{2\mathcal{F}(\phi(s) - \phi(s + \delta_{dl}))}{\mathcal{R}T} \right] = a_{O_{O,i}}^{\times} \frac{K_{O_s^{2-}}}{K_{O_i^{2-}}} \exp \left[\frac{2\mathcal{F}(\phi_{ad} - \phi_{io})}{\mathcal{R}T} \right] \quad (3.32)$$

Where ϕ_{io} is the electrostatic potential in the ionic conductor, just outside the electric double-layer, and ϕ_{ad} is the electrostatic potential at the site of adsorbed species (*i.e.*, the potential in the adsorbed monolayer), according to Fig. 3.3. Thus, from the equations above one has

$$\begin{aligned} \mathcal{R}T \ln K_{O_i^{2-}} &= \mathcal{R}T \left(\ln a_{O_{O,i}}^{\times} - \frac{1}{2} \ln a_{O_2} - 2 \ln a_{e'} \right) + 2\mathcal{F} \left[\phi_{e'}(r = s - \delta_{dl}) - \phi_{O_{O}}^{\times}(r = s + \delta_{dl}) \right] \\ &= \mathcal{R}T \ln \frac{a_{O_{O,i}}^{\times}}{a_{e'}^2 \sqrt{a_{O_2}}} + 2\mathcal{F} \left[\phi_{e'}(r = s - \delta_{dl}) - \phi_{O_{O}}^{\times}(r = s + \delta_{dl}) \right] \\ \Rightarrow K_{O_i^{2-}} &= \frac{a_{O_{O,i}}^{\times}}{a_{e'}^2 \sqrt{a_{O_2}}} \exp \left(\frac{2\mathcal{F}\Delta\phi_i}{\mathcal{R}T} \right) \end{aligned} \quad (3.33)$$

Defining the activity for the surface species as^[33]:

$$a_{O_{O,s}}^{\times} = \Theta_{O_{ad}^{2-}} \Gamma_{elde} / \Gamma_{elde}^{\dagger} \quad (3.34)$$

Where $\Theta_{O_{ad}^{2-}}$ is the dimensionless surface site (coverage) fraction occupied by oxide ad-ions; Γ_{elde} is the actual surface site density available in the electrode phase (in moles cm⁻²); and

$\Gamma_{elde}^{\ddagger}$ is a fixed standard state site density. For simplicity sake, it is considered that $\Gamma_{elde} \cong \Gamma_{elde}^{\ddagger}$ and $a_{e'} \cong 1$, which then yields

$$\Theta_{O_{ad}^{2-}} = \sqrt{p_{O_2}} K_{O_s^{2-}} \exp \left[-\frac{2F(\Delta\phi_i + \Delta\chi)}{\mathcal{R}T} \right] \quad (3.35)$$

Where

$$\begin{aligned} \Delta\phi_i + \Delta\chi &= [\phi_{e'}(r = s - \delta_{dl}) - \phi_{O_o^\times}(r = s + \delta_{dl})] + [\phi_{io} - \phi_{ad}] \\ &= [\phi_{e'}(r = s - \delta_{dl}) - \phi_{O_o^\times}(r = s)] + [\phi_{O_o^\times}(r = s + \delta_{dl}) - \phi_{O_o^\times}(r = s + \delta_{dl})] \\ &= \phi_{e'}(r = s - \delta_{dl}) - \phi_{O_o^\times}(r = s) = \Delta\phi_s \end{aligned} \quad (3.36)$$

For illustration purposes, one can express $\Delta\phi_s$ (potential difference between the electronic conductor and the adsorbed layer) using the following result from [111, 116]:

$$\Delta\phi_s = \Theta_{O_{ad}^{2-}} n_{ad} \frac{|e|}{\mathcal{C}_{dl}} \left(\frac{\text{occupied surface sites}}{\text{available surface sites}} \right) \left(\frac{\text{available surface sites}}{\text{cm}^2} \right) \left(\frac{\text{C}}{\mu\text{F cm}^{-2}} \right) \quad (3.37)$$

Where n_{ad} indicates the number of available surface sites and $\mathcal{C}_{dl}$ denotes the corresponding double-layer capacitance. Equation (3.37) is a phenomenological “mimic” of the result for a parallel capacitor, wherein the ratio “number of charges / capacitance” gives the potential difference (voltage) of that capacitor (“the stored electrical charge”). Therefore, for oxide-ions as the main $\Delta\phi_s$ determining species, the surface coverage for the oxygen reduction $1/2 O_2 + 2e^- \rightleftharpoons O_{ad}^{2-}$ can be now calculated (at equilibrium) as

$$\Theta_{O_{ad}^{2-}} = \sqrt{p_{O_2}} K_{O_s^{2-}} \exp \left[-\frac{2F}{\mathcal{R}T} \Theta_{O_{ad}^{2-}} (\Delta\phi_s)_{max} \right] \quad (3.38)$$

Where

$$(\Delta\phi_s)_{max} = \frac{n_{ad} |e|}{\mathcal{C}_{dl}} \quad (3.39)$$

Is the surface potential step when O_{ad}^{2-} reaches full site occupancy. In the derivation of Eq. (3.24a) it was assumed that the surface coverage $\Theta_{O_{ad}^{2-}}$ is proportional to $\sqrt{p_{O_2}}$, instead of following a Langmuir-type dissociative adsorption kinetics, *i.e.* $\Theta_{O_{ad}^{2-}} / (1 - \Theta_{O_{ad}^{2-}}) \propto \sqrt{p_{O_2}}$, which is commonly used when site restriction plays a role³. If, however, one now considers $\Gamma_{elde} / \Gamma_{elde}^{\ddagger} \cong 1 / (1 - \Theta_{O_{ad}^{2-}})$ so that the chemical activity of the adsorbed oxide ion is expressed by $a_{O_o^\times, s} = \Theta_{O_{ad}^{2-}} / (1 - \Theta_{O_{ad}^{2-}})$, Eq. (3.38) now reads

³ Also note that in Eq. (3.27) there is no species representing the equivalent to a “an open site” species, which would lead to the additional factor $1 - \Theta_{O_{ad}^{2-}}$ in the expression for the adsorption isotherm^[33].

$$\Theta_{O_{ad}^{2-}} = (1 - \Theta_{O_{ad}^{2-}}) \sqrt{p_{O_2}} K_{O_s^{2-}} \exp \left[-\frac{2F}{RT} \Theta_{O_{ad}^{2-}} (\Delta\phi_s)_{max} \right] \quad (3.40)$$

Differently from what is proposed by Eq. (3.40), the assumption made by standard literature relationships for $\Theta \sim p_{O_2}$, which disregards the effect of double-layer's potential step, is reasonable as long as neutral surface species are the only considered species. This is because charged oxygen species such as O_{ad}^{2-} experience an additional energy contribution due to the electrostatic surface potential step^[111]. Nevertheless, if the presence of O_{ad}^{2-} is predominately small, the corresponding potential step $\Delta\phi_s$ is small as well. In this case, electrostatics plays a minor role and O_{ad}^{2-} behaves almost like an uncharged particle. Furthermore, if the surface coverage hardly exceeds 10–20%, the assumption of site restrictiveness for O_{ad}^{2-} can be neglected (*i.e.*, assuming a Langmuir dissociative adsorption kinetics^[33] is not justified in this case).

Figure 3.4: surface coverage of O_{ad}^{2-} versus oxygen partial pressure for different potential steps $(\Delta\phi_s)_{max}$ and equilibrium constants $K_{O_s^{2-}}$, with $\mu_{e'} = \text{const.}$ and $T = 1073 \text{ K}$. Note that for $(\Delta\phi_s)_{max} > 0.25 \text{ V}$ (*i.e.*, when electrostatics becomes important) the surface coverage varies only slightly with p_{O_2} , more so when $p_{O_2} \geq 0.15 \text{ bar}$. Where it was not explicitly indicated, $K_{O_s^{2-}} = 2.25 \text{ bar}^{-1/2}$.

From Fig. 3.4 it is noted that for surface potential steps $(\Delta\phi_s)_{max}$ above 0.25 V the surface coverage of O_{ad}^{2-} becomes virtually insensitive with respect to p_{O_2} , within the range of oxygen partial pressures usually found in SOFC cathodes ($0.1 \leq p_{O_2} \leq 0.21$). It is also verified

that for low surface coverages, which is the typical situation when electrostatics becomes important, the $\Theta_{O_{ad}^{2-}}$ is proportional to $\sqrt{p_{O_2}}$ and thus the restriction of adsorption sites becomes unimportant. That is, the results predicted by Eq. (3.38) and Eq. (3.40) tend to collapse. On the other hand, as the value of $(\Delta\phi_s)_{max}$ becomes progressively smaller, $\Theta_{O_{ad}^{2-}}$ varies greatly with p_{O_2} and the adsorption behavior tends to a purely Langmuir-type description⁴, simply given as

$$\Theta_{O_{ad}^{2-}} = \frac{\sqrt{p_{O_2} K_{eq}}}{1 + \sqrt{p_{O_2} K_{eq}}} \quad (3.41)$$

Where $\sqrt{K_{eq}} = K_{O_s^{2-}}$ is the equilibrium constant for a dissociative adsorption reaction, when it is written in the more usual form $O_{2(g)} + 2Ad_{(s)} \rightleftharpoons 2O_{(s)}$, where $Ad_{(s)}$ and $O_{(s)}$ represent a free (open) adsorption site and an oxygen ad-atom on the cathode surface, respectively.

Estimating reasonable values for $(\Delta\phi_s)_{max}$ is not a straightforward task, because the prescription of values to the phenomenological parameters n_{ad} and $\mathcal{C}_{dl}$ is not without difficulties, due to the macroscopic degeneracy^[117] of the adopted continuum-level description (see §§2.3.2). One can find values in the literature for both n_{ad} and $\mathcal{C}_{dl}$ (e.g., see [112, 118, 119, 120]), but these cannot be rigorously and directly compared to the ones appearing in Eq. (3.37). For example, one may choose $\mathcal{C}_{dl}$ to lie between 10 $\mu\text{F}/\text{cm}^2$ (i.e., a representative value close to the conditions of vacuum permittivity^[111], admitting an arbitrary distance between spaced charges around 1 Å), and a supposed maxima of 40 $\mu\text{F}/\text{cm}^2$ ^[119]. By its turn, the number of available surface sites may be expressed as

$$n_{ad} = \mathcal{N}_a \Gamma_{elde(tpb)} \quad (3.42)$$

where $\mathcal{N}_a$ is the Avogadro number and $\Gamma_{elde(tpb)}$ is the density of “active” surface sites near the TPB region. That is, it represents just a fraction of the total surface site density Γ_{elde} available over the entire electrode phase. It is a fraction because only those sites sufficiently close to the TPB hot spot will be considered “active” for the adsorption of charged species, which are then able to subsequently undergo the electrochemical reduction reaction at the TPB (see Fig. 3.5).

⁴ In Fig. 3.4, compare the curve “0.0 V - Eq. (3.40)” to “Langmuir ($K_{O_s^{2-}} = 2.25 \text{ bar}^{-1/2}$)” and note that they coincide, obviously.

Figure 3.5: electrocatalytic and transport processes in a composite (e.g., LSM/YSZ) cathode limited by competing surface diffusion and adsorption processes (figure by the author based on descriptions from [112, 121]).

In Fig. 3.5, L_s is some characteristic length of the electrode microstructure, here referred to as a “surface diffusion length”. The characteristic length δ_s , confining the active region for adsorption/diffusion processes, may be defined as follows^[112]:

$$\delta_s = \sqrt{D_s / k_o} \quad (3.43)$$

Where D_s is a surface diffusion coefficient and k_o is a rate constant characteristic of the adsorption reaction, which can be evaluated from the following governing equation for oxygen ad-atoms being transported on the electrode surface, at steady state:

$$\frac{\partial \Theta_{O_{ad}^{2-}}}{\partial t} = 0 = D_s \frac{\partial^2 \Theta_{O_{ad}^{2-}}}{\partial y^2} + k_{ads,f} \sqrt{p_{O_2}} (1 - \Theta_{O_{ad}^{2-}}) - k_{ads,r} \Theta_{O_{ad}^{2-}} \quad (3.44)$$

Equation (3.44) may be rewritten as

$$-\frac{D_s}{k_{ads,r}} \frac{\partial^2 \Theta_{O_{ad}^{2-}}}{\partial y^2} = -\Theta_{O_{ad}^{2-}} (K_{O_s^{2-}} \sqrt{p_{O_2}} + 1) + K_{O_s^{2-}} \sqrt{p_{O_2}} \quad (3.45)$$

Where $K_{O_s^{2-}} = k_{ads,f} / k_{ads,r}$. By defining the following characteristic length

$$Y = \sqrt{\frac{D_s}{k_{ads,r} K_{O_s^{2-}} \sqrt{p_{O_2}}}} \quad (3.46)$$

Equation (3.45) is rearranged as

$$Y^2 \frac{\partial^2 \Theta_{O_{ad}^{2-}}}{\partial y^2} = \Theta_{O_{ad}^{2-}} \left(1 + \frac{1}{K_{O_s^{2-}} \sqrt{p_{O_2}}} \right) - 1 = \frac{K_{O_s^{2-}} \sqrt{p_{O_2}} (\Theta_{O_{ad}^{2-}} - 1) + \Theta_{O_{ad}^{2-}}}{K_{O_s^{2-}} \sqrt{p_{O_2}}} \quad (3.47)$$

Assuming the condition of low surface coverage, $\Theta_{O_{ad}^{2-}} \ll 1$, according to Fig. 3.4, Eq. (3.47) is further simplified, yielding

$$Y^2 \frac{\partial^2 \Theta_{O_{ad}^{2-}}}{\partial y^2} = \frac{\Theta_{O_{ad}^{2-}}}{K_{O_s^{2-}} \sqrt{p_{O_2}}} - 1 \quad (3.48)$$

Equation (3.48) is a nonhomogeneous, 2nd order ODE which can be analytically solved by traditional methods (see **APPENDIX A**), subjected to the following boundary conditions:

$$\Theta_{O_{ad}^{2-}} \Big|_{y=0} = \Theta_{O_{ad}^{2-}}^{TPB} \quad (3.49)$$

$$\frac{\partial \Theta_{O_{ad}^{2-}}}{\partial y} \Big|_{y=L_s} = 0 \quad (3.50)$$

The Newman-type boundary condition, Eq. (3.50), represents a no-flux condition at the plane $y = L_s$, according to Fig. 3.5. The Dirichlet-type boundary condition, Eq. (3.49), represents the relationship between the surface potential step ($\Delta\phi_s$) and surface coverage at the TPB. In order to calculate $\Theta_{O_{ad}^{2-}}^{TPB}$, either Eq. (3.38) or (3.40) can be used. One could now solve Eq. (3.48)-(3.50) in order to find δ_s , using some “penetration criterion”, such as $\Theta_{O_{ad}^{2-}}(\delta_s)/\Theta_{O_{ad}^{2-}}(\delta_s + \delta y) < 0.01$, where $\delta y \ll \delta_s$ is some arbitrary integration step. For illustrative purposes, however, the interest here is to find a straightforward way to calculate $\Gamma_{elde(tpb)}$ (to be used in Eq. (3.42)), thus it is best to avoid this numerical burden at this time.

As mentioned above, δ_s may be calculated from Eq. (3.43), but one needs to determine a suitable definition for k_o . The solution of Eq. (3.48), according to the boundary conditions Eq. (3.49) and (3.50), can provide the profile of surface coverage and from this profile one should be able to determine a constitutive relation for k_o . Here it is suggested a relation based on the following analytical solution of Eq. (3.48) (see **APPENDIX A** for its proof):

$$\Theta_{O_{ad}^{2-}}(y) = K_{O_s^{2-}} \sqrt{p_{O_2}} \left[1 - \frac{2\mathcal{F}}{RT} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \frac{\cosh\left((L_s - y) \sqrt{\frac{1}{Y_*^2}}\right)}{\cosh\left(L_s \sqrt{\frac{1}{Y_*^2}}\right)} \right] \quad (3.51)$$

where

$$Y_*^2 = \frac{Y^2}{K_{O_2}^2 - \sqrt{p_{O_2}}} \quad (3.52)$$

The result of Eq. (3.51) suggests that

$$\delta_s = \sqrt{Y_*^2} = \sqrt{\frac{D_s}{k_{ads,r} K_{O_2}^2 - \sqrt{p_{O_2}}}} = \sqrt{D_s/k_0} \quad \therefore k_0 = k_{ads,r} K_{O_2}^2 - \sqrt{p_{O_2}} \quad (3.53)$$

Therefore, using Eq. (3.53) n_{ad} may be now expressed as (assuming that $\Gamma_{elde(tpb)} \leq \Gamma_{elde}$)

$$\begin{cases} n_{ad} = \mathcal{N}_a \Gamma_{elde(tpb)} = \mathcal{N}_a \Gamma_{elde} \delta_s^2 \lambda_{tpb}, & \text{if } \delta_s \leq L_s \\ n_{ad} = \mathcal{N}_a \Gamma_{elde(tpb)} = \mathcal{N}_a \Gamma_{elde} L_s^2 \lambda_{tpb}, & \text{if } \delta_s > L_s \end{cases} \quad (3.54)$$

Where λ_{tpb} is the TPB length density^[7, 17, 122, 123] (e.g., m/m³), which may be also interpreted as being the number of TPB “hot spots” (or “active sites”) per unit area; and L_s , the “surface diffusion length” (actually, a microstructural parameter), which may be defined as the median of the LSM/pore interface length divided by two^[112] and it can be estimated from SEM images using image processing softwares, such as the well-known ImageJ^[124, 125]. An interpretation for the meaning of Eq. (3.54) is depicted in Fig. 3.6 below and it can be summarized by the following: the term $\mathcal{N}_a \Gamma_{elde} \delta_s^2$ represents the number of adsorption sites that are “reachable” from within a single active zone (“unit cell”) of area δ_s^2 . Multiplying it by λ_{tpb} will scale the number of sites to all regions (“unit cells”) that are each of them centered on every available TPB point.

Figure 3.6: simplified depiction of active adsorption sites near TPB “hot spots” (figure by the author).

As mentioned in the foregoing paragraphs, $\mathcal{C}_{dl}$ typically lies between 10 $\mu\text{F}/\text{cm}^2$ and 40 $\mu\text{F}/\text{cm}^2$. Due to the lack of a more appropriate criteria, one may choose the middle value

as the compromise between these two extremes, although the choice should have been in the direction of underestimating⁵ $(\Delta\phi_s)_{max}$; that is, to choose $C_{dl} = 40 \mu\text{F}/\text{cm}^2$. However, here $C_{dl} = 25 \mu\text{F}/\text{cm}^2$ is selected. Other chosen values are: $\Gamma_{elde} = 2.5 \times 10^{-9} \text{ mol}/\text{cm}^2$ [83, 118, 119, 121], $\lambda_{tpb} = 1.1 \mu\text{m}^{-2}$ [17, 122, 123], $D_s = 5 \times 10^{-9} \text{ cm}^2/\text{s}$ [112, 126, 127], $k_{ads,r} = 5 \text{ s}^{-1}$ [112, 128, 129, 130, 131, 1], $K_{O_s^{2-}} = 2.25 \text{ bar}^{-1/2}$. Although these proposed values are expected to fall within a typical range for cathodes where perovskite oxides of ionic character are employed, they certainly convey an inordinate level of arbitrariness, which is only acceptable for the purpose of an illustrative exercise⁶. It should be also emphasized that in this study oxygen surface exchange is assumed to occur, predominately, via surface oxygen ions (*i.e.*, O^- as the dominant reaction species) and that D_s is the surface diffusion coefficient of adsorbate in the low-coverage limit.

Using the above parameter values, n_{ad} was calculated as $1.61 \times 10^{14} \text{ sites}/\text{cm}^2$ at conditions of $p_{O_2} = 0.21 \text{ bar}$ and $T = 1073 \text{ K}$, for which $(\Delta\phi_s)_{max} = 1.03 \text{ V}$. In Fig. 3.4, a curve using these parameters was indicated as "Varying $(\Delta\phi_s)_{max}$ - Eq. (3.40), (3.54)". It can be seen that this curve presents a different behavior, where it now "intersects the other curves" because $(\Delta\phi_s)_{max}$ is no longer a fixed value, as it varies with respect to $n_{ad} = n_{ad}(p_{O_2})$. Thus, when inspecting Fig. 3.4 with regard to the curve "Varying $(\Delta\phi_s)_{max}$ - Eq. (3.40), (3.54)" one finds that $\theta_{O_{ad}^{2-}}$ varies from $\cong 0.11$ up to $\cong 0.16$ in the interval between $p_{O_2} = 0.1 \text{ bar}$ to $p_{O_2} = 0.21 \text{ bar}$. If it is assumed that the overall change in the activity ($a_{O_{O,i}^{2-}}$) of bulk oxygen ions (at the vicinity of electrode/electrolyte interface) varies in the same proportion ($\approx 30\%$ of relative variation), one obtains a concentration polarization⁷ ($\eta_{C,ca}$) roughly of the order of $\cong 17 \text{ mV}$. Considering a narrow interval, from $p_{O_2} = 0.15 \text{ bar}$ up to 0.21 bar , the concentration polarization caused by surface ad-ions would be now $\cong 6 \text{ mV}$. If, on the other hand, one selects any of the other curves represented by Eq. (3.40), with $(\Delta\phi_s)_{max}$ fixed down to 0.5 V , the variation of $\theta_{O_{ad}^{2-}}$ is virtually negligible (considering the same interval of oxygen partial pressures) and thus $\eta_{C,ca} \approx 0$ when due to surface ad-ions.

⁵ Here one tries to not overestimate the importance of the surface polarization effect on the adsorption process of oxygen ions, by "underestimating" the value of $(\Delta\phi_s)_{max}$. For high values of $(\Delta\phi_s)_{max}$ the ascending curve $\theta_{O_{ad}^{2-}}$ vs p_{O_2} becomes a plateau, *i.e.* $\theta_{O_{ad}^{2-}}$ becomes insensible to oxygen partial pressure. The increase of $(\Delta\phi_s)_{max}$ implies a reduction of oxygen adsorption energy and thus an effective enhancement of adsorption kinetics. The relation $\theta_{O_{ad}^{2-}} = \theta_{O_{ad}^{2-}}(p_{O_2})$, however, is the main effect under study in section.

⁶ The level of uncertainty regarding the effective rate constant $k_{ads,r}$ for the desorption reaction (*i.e.*, reverse reaction of $O_{2(g)} + 2Ad_{(s)} \rightleftharpoons 2O_{(s)}$) is particularly worrisome^[129, 131].

⁷ Evaluated using Eq. (3.14) with support of Eq. (3.32) and (3.34), and also assuming that bulk mass action constants ($K_{O_s^{2-}}$ and $K_{O_i^{2-}}$) remain invariant with respect to p_{O_2} .

The above conclusions are to a great extent speculative in nature, because they are compromised by two main limitations: firstly, the uncertainty concerning the parameter values that have been chosen in the study; secondly, the intrinsic limitation of a mean-field approximation when using a phenomenological kinetics description for nanoscale-driven heterogeneous catalytic processes^[55, 132, 133]. Furthermore, it is certainly difficult to conceive an experimental setup, or a “thought experiment” for that matter, where concentration-induced polarizations caused by adsorbed surface species could be actually measured or somewhat quantified. For instance, changes in the oxygen partial pressure can also lead to other “second order” voltage losses, such as those related to electronic leakage in ionic-conducting materials^[8], whose individual effect would be troublesome to identify and measure.

3.4 Concentration-Induced Nernstian Losses

3.4.1 Losses along Electrode's Through-Plane Direction

Nernstian losses are simply the cell voltage decrease across the electrode thickness (*i.e.*, along electrode's through-plane direction, see Fig. 3.2), which may be predicted by Eq. (3.3) in the situations when the reactant concentration at the TPB is decreased relative to the bulk concentration; and/or the product concentration at the TPB is increased relative to the bulk concentration. If the difference in concentration is assumed to stem from diffusion-controlled transport, at steady state, the flux of reactants and products down the concentration gradients should match the consumption/production rate of reactants/products at the TPB:

$$i = z_e \mathcal{F} \vec{j}_k \cdot \vec{n} \quad (k = \text{electroactive reactant or product}) \quad (3.55)$$

where i is the cell operating current density; $\vec{j}_k$ is the diffusive molar flux of a reactant towards the TPB (or the diffusive molar flux of a product away from the TPB); and $\vec{n}$ is the (normal) outward pointing unit vector to the electrode/electrolyte interface. Introducing a simple Fickian definition for the diffusion flux in the case of H_2 (*i.e.*, anode), Eq. (3.55) may be written as

$$\begin{aligned} i &= z_{e,an} \mathcal{F} [-\mathcal{D}_{H_2}^{\text{eff}} \nabla_z (C_{H_2})] \cong -2 \mathcal{F} \mathcal{D}_{H_2}^{\text{eff}} \frac{(C_{H_2,an/elyt} - C_{H_2,bulk})}{\delta_{diff,an}} \\ \Rightarrow C_{H_2,an/elyt} &\cong C_{H_2,bulk} - \frac{i \delta_{diff,an}}{2 \mathcal{F} \mathcal{D}_{H_2}^{\text{eff}}} \end{aligned} \quad (3.56)$$

where $\mathcal{D}_{H_2}^{\text{eff}}$ is an effective (or rather, an experimentally representative) diffusivity for H_2 within the anode porous layer. This simplified equation indicates that the reactant concentration in the electrode/electrolyte interface depends on i , $\delta_{diff,an}$, and $\mathcal{D}_{H_2}^{\text{eff}}$. Thus, as the value of i increases, the reactant depletion effect is amplified. That is, the higher the current density, the

worse the concentration-induced loss. Equation (3.56) also states that this concentration loss can be minimized if the diffusion layer thickness is reduced or the diffusivity is somehow increased. Analytical expressions such as Eq. (3.56), which employ physically measurable parameters, have been used in the SOFC literature extensively to determine anodic or cathodic concentration polarizations^[82, 134] (see also **Chapter 4**). These expressions vary significantly in both their form and prediction range, depending on, for instance, the number of parameters considered, the constitutive relation used for the diffusive flux (*e.g.*, “Fick’s law”, “generalized Fick’s law”, “Maxwell-Stefan”), if the fuel and oxidant inlet gas streams were admitted pure or diluted with some inert gas, and so on.

More often than not, analytical expressions that are employed to evaluate concentration polarization make use of an important parameter, commonly termed as the limiting current density (i_L), to describe both anode ($i_{L,an}$) and cathode ($i_{L,ca}$) mass transfer processes. The anode-limiting current density is usually defined^[76, 81] as the current density at which the interfacial fuel partial pressure at the anode/electrolyte interface (*i.e.*, at TPBs) is zero (the cell is starved of fuel). Similarly, the cathode-limiting current density is defined as the current density at which the interfacial oxygen partial pressure at the cathode/electrolyte interface is zero (the cell is starved of oxidant). It is a material characteristic of the SOFC and provides a measure of the resistance to concentration polarizations (a higher i_L implies potentially lower losses). The limiting current density can be calculated from Eq. (3.56) by setting $C_{H_2,an/elyt} = 0$:

$$i_{L,an} \cong \frac{z_{e,an} \mathcal{F} D_{H_2}^{eff} C_{H_2,bulk}}{\delta_{diff,an}} \cong \frac{2 \mathcal{F} D_{H_2}^{eff} C_{H_2,bulk}}{\delta_{diff,an}} = \frac{2 \mathcal{F} D_{H_2}^{eff} p_{H_2,bulk}}{RT \delta_{diff,an}} \quad (3.57)$$

And similarly for the cathode:

$$i_{L,ca} \cong \frac{z_{e,ca} \mathcal{F} D_{O_2}^{eff} C_{O_2,bulk}}{\delta_{diff,ca}} \cong \frac{4 \mathcal{F} D_{O_2}^{eff} C_{O_2,bulk}}{\delta_{diff,ca}} = \frac{4 \mathcal{F} D_{O_2}^{eff} p_{O_2,bulk}}{RT \delta_{diff,ca}} \quad (3.58)$$

Analogous expressions can be developed to account for product accumulation effects, in lieu of considering only reactant depletion effects. Here, for simplicity, the above analytical expressions consider only depletion effects. The limiting current density represents a theoretical upper limit for mass transport (see Fig. 3.7), as the SOFC cannot sustain higher current densities than that which causes the fuel/oxidant concentration to fall to near zero at TPBs. Even though Fig. 3.7 seemingly suggests that the limiting current would constitute a “distant limit” for SOFC operation, it is important to stress that concentration losses can be significant even at lower current densities, contrary to what is generally acknowledged in the literature.

Figure 3.7: sample polarization curve showing major losses and the maximum (theoretical) current density (figure by the author).

The concentration polarization can be expressed in terms of the limiting current density. Using Eq. (3.56) and (3.57), the ratio $C_{H_2,bulk}/C_{H_2,an/elyt}$ may be written as:

$$\frac{C_{H_2,bulk}}{C_{H_2,an/elyt}} \cong \frac{(i_{L,an} \delta_{diff,an}/z_{e,an} \mathcal{F} \mathcal{D}_{H_2}^{eff})}{(i_{L,an} \delta_{diff,an}/z_{e,an} \mathcal{F} \mathcal{D}_{H_2}^{eff}) - (i \delta_{diff,an}/z_{e,an} \mathcal{F} \mathcal{D}_{H_2}^{eff})} \cong \frac{i_{L,an}}{i_{L,an} - i} \quad (3.59)$$

Substituting this result into Eq. (3.56) and ignoring the effect from product accumulation:

$$\eta_{C,an} \cong \frac{\mathcal{R} T}{z_{e,an} \mathcal{F}} \ln \left(\frac{i_{L,an}}{i_{L,an} - i} \right) \quad (3.60)$$

An analogous procedure holds for the cathode as well:

$$\eta_{C,ca} \cong \frac{\mathcal{R} T}{z_{e,ca} \mathcal{F}} \ln \left(\frac{i_{L,ca}}{i_{L,ca} - i} \right) \quad (3.61)$$

In Eq. (3.60) or (3.61), as the operating current density approaches its limiting value, that is when $i \rightarrow i_{L,an}$ (or $i \rightarrow i_{L,ca}$), the term $\eta_{C,an}$ (or $\eta_{C,ca}$) approaches infinity (with distinct lateral limits, i.e. there is a jump discontinuity). However, the maximum value of η_{conc} is physically limited by the OCV. Thus, the maximum current density will be always less than i_L . Moreover, other voltage losses (e.g., ohmic and activation losses) may degrade the SOFC operating voltage to zero, well before i_L is ever reached.

Here again, expressions such as equations (3.60) and (3.61) can also vary significantly in both their form and prediction scope (see §§4.4). At first glance, these expressions may seem to dictate a general asymptotic behavior of SOFCs. However, this latter observation is not founded on fundamental arguments. Equations (3.60) and (3.61) are just observed phenomenological statements that were verified by their empirical consequences, in well-

defined experimental settings. This implies that both interpretation and use of such formulae are (or should be) restricted to those experimental conditions. For instance, even the ubiquitous assumption that $C_{H_2,an/elyt}$ drops to zero as $i \rightarrow i_{L,an}$ is not always correct, sometimes leading to unphysical approximations^[135]. Furthermore, up to this moment, there are no reliable quantitative experiments carried out to investigate the effects on correlated processes that occur very near this seeming stringent limit, such as space charge^[136] and interfacial strain effects^[137], which could also influence gas transport mechanisms.

3.4.2 Losses along Mean Flow Direction (Reactant Depletion in Gas Channels)

There is another cell operation-related effect that (sometimes) is not attributed (directly) to concentration polarization, but it is an effect that is nonetheless a form of concentration-induced voltage loss. If the gas channel inlet stream is not pure fuel/oxidant, there is an irreversible mixing of gases along the channel's mean flow direction, as progressively more fuel/oxidant is used in the chemical reactions (e.g., bulk flow gets diluted in respect to fuel/oxidant), causing the cell voltage to fall (see Fig. 3.8). In the case of a fuel channel, the leaner the mixture, the lower is the available cell voltage (see Fig. 3.9). Therefore, in real operating situations, the fuel can never be fully consumed in the SOFC itself and some of it must be left in the anode exhaust stream^[4, 13].

Figure 3.8: straight fuel channel of a SOFC anode and the hydrogen concentration profile along that channel, here represented through a simplified quasi-2D model (see also §§4.3.2 and §§4.10.2) (figure by the author)

This mixing effect by fuel utilization is a critical aspect of SOFC performance, as it can strikingly reduce the electric power available. As this effect is an irreversible thermodynamic

process, a SOFC under the assumption of a quasi-static operation is restricted to the limiting case of a vanishing fuel utilization factor, that is, $U_{fu} \rightarrow 0$ (where U_{fu} is the ratio of the spent fuel to the inlet fuel). The voltage loss (reduction of E_{rev}^{bulk}) can be calculated by expressing U_{fu} as a function of the change in species concentration within gas channel (see Fig. 3.9).

Figure 3.9: voltage curves showing how E_{rev}^{bulk} depends on U_{fu} and temperature (picture modified from [4]).

An important behavior to consider, regarding possible voltage losses along the mean flow direction, is the variation of the Nernst potential for different fuels-oxidant systems as a function of fuel utilization U_{fu} . Figure 3.10 illustrates this behavior for three fuels (H_2 , CH_4 , and C_4H_{10}) using Eq. (3.62) which will be described below.

Figure 3.10: Nernst potential calculated for distinct fuels-air systems as a function of the of fuel utilization (U_{fu}). As the fuel is converted to its stoichiometric products, the fuel is further diluted in the gas mixture. For these hypothetical SOFC systems, the oxygen in the cathode compartment was assumed not to be depleted, *i.e.* potentials have been calculated presuming no depletion of oxygen in the air mixture (picture from [138]).

As shown in Fig. 3.10, Nernst potentials are highest for heavier hydrocarbons, if their direct electrochemical oxidation^[140, 141, 142] is assumed, *i.e.* without the need of a prior reforming step for the obtainment of a hydrogen gas mixture. On the other hand, the Nernst potential for hydrogen is the most reduced as a function of fuel depletion.

Based on the nomenclature proposed by Zhu and Kee proposed in [138, 139], one can express the chemical potential balance at open circuit conditions (*i.e.*, using the Nernst equation) as:

$$E_{rev} = E^\ominus + \frac{RT}{z_e \mathcal{F}} \sum_{k=1}^{N_{spe}} [v'_{fu,k} + v'_{ox,k} - (v''_{fu,k} + v''_{ox,k})] \ln \left(\frac{p_k}{p_\ominus} \right) \quad (3.62)$$

Where N_{spe} is the total number chemical species (gaseous, surface, or solid bulk species); $v'_{fu,k}$ and $v'_{ox,k}$ are the stoichiometric coefficients for the k -th reactant in the fuel and air channels, respectively; $v''_{fu,k}$ and $v''_{ox,k}$ are the stoichiometric coefficients for the k -th product in the fuel and air channels, respectively; $E^\ominus$ is now expressed as $E^\ominus = 1/(z_e \mathcal{F}) \sum_{k=1}^{N_{spe}} [v'_{fu,k} + v'_{ox,k} - (v''_{fu,k} + v''_{ox,k})] \mu_k^\ominus$. As an alternative to using species partial pressures, the Nernst equation can also be represented in terms of the species molar concentrations C_k as:

$$\begin{aligned} E_{rev} &= E^\ominus + \frac{RT}{z_e \mathcal{F}} \sum_{k=1}^{N_{spe}} [v'_{fu,k} + v'_{ox,k} - (v''_{fu,k} + v''_{ox,k})] \ln \left(\frac{C_k}{C_{ref}} \right) + \\ &\quad + \frac{RT}{z_e \mathcal{F}} \ln \left(\frac{RT C_{ref}}{p_\ominus} \right) \sum_{k=1}^{N_{spe}} [v'_{fu,k} + v'_{ox,k} - (v''_{fu,k} + v''_{ox,k})] \\ \Rightarrow E_{rev} &= E^\ominus + \frac{RT}{z_e \mathcal{F}} \sum_{k=1}^{N_{spe}} [v'_k - v''_k] \ln C_k + \frac{RT}{z_e \mathcal{F}} \ln \left(\frac{RT}{p_\ominus} \right) \sum_{k=1}^{N_{spe}} [v'_k - v''_k] \\ \Rightarrow E_{rev} &= E^\ominus + \frac{RT}{z_e \mathcal{F}} \left[\sum_{k=1}^{N_{spe}} v_k \ln C_k + \ln \left(\frac{RT}{p_\ominus} \right) \sum_{k=1}^{N_{spe}} v_k \right] \end{aligned} \quad (3.63)$$

Where $v'_k = v'_{fu,k} + v'_{ox,k}$ and $v''_k = v''_{fu,k} + v''_{ox,k}$; thus, the net stoichiometric coefficient of the k -th species is generally defined as $v_k = v''_k - v'_k$. Here C_{ref} is some arbitrary constant.

3.5 Concentration-Induced Kinetic Losses

The concentration gradients of electroactive species can also impact the kinetics of electrode processes^[68], even though this effect is seldom reckoned as a concentration polarization. It occurs if the rate law, which is used to describe the kinetics of electrochemical reactions, takes into consideration the concentration of these species. This effect may be

better understood by comparing the following BVEs (see also discussion in §2.3.4), which are commonly used to model electrode kinetics, e.g. for the anode case:

$$i = i_{*,ref} \left[\left(\frac{C_{H_2,an/elyt}}{C_{H_2,ref}} \right)^a \exp \left(\frac{\alpha_a \mathcal{F} z_{e,an} \eta_{A,an}^{TPB}}{\mathcal{R}T} \right) - \left(\frac{C_{H_2O,an/elyt}}{C_{H_2O,ref}} \right)^b \exp \left(- \frac{\alpha_c \mathcal{F} z_{e,an} \eta_{A,an}^{TPB}}{\mathcal{R}T} \right) \right] \quad (3.64)$$

$$i = i_{0,ref} \left[\exp \left(\frac{\alpha_a \mathcal{F} z_{e,an} \eta_{A,an}}{\mathcal{R}T} \right) - \exp \left(- \frac{\alpha_c \mathcal{F} z_{e,an} \eta_{A,an}}{\mathcal{R}T} \right) \right] \quad (3.65)$$

Where $C_{H_2,ref}$ and $C_{H_2O,ref}$ are adopted reference concentrations; $i_{*,ref}$ is the exchange current density evaluated at those reference concentrations; α_a and α_c are the anodic and cathodic transfer coefficients, respectively, for the hydrogen oxidation reaction on the anode side; the exponential parameters a and b are known experimental parameters; and $\eta_{A,an}^{TPB}$ is the activation overvoltage referred to the gas concentration at the TPB conditions. The difference between Eq. (3.64) and (3.65) is clear. The first one explicitly considers the influence from the concentration of reactants and products at anode/electrolyte reaction sites, whereas the second form does not.

A similar expression to Eq. (3.60) can be obtained to account for the “kinetic loss” in the case the reactant concentration at the TPB is decreased relative bulk concentration. Accordingly, the bulk concentration $C_{H_2,bulk}$ should be used in the Eq. (3.64), in place of $C_{H_2,an/elyt}$. The goal here is just to take this effect (“concentration difference between the bulk and the TPB”) out from the activation polarization ($\eta_{A,an}$) and consider this effect as an additional term inside the concentration polarization ($\eta_{C,an}$). This is similar to what have been discussed about reversible voltages (i.e., E_{rev}^{TPB} versus E_{rev}^{bulk}) during the definition of concentration polarization. For illustrative purposes, such derivation can be realized using a simplified BVE, only valid for the high-current-density region (within which the cathodic term in Eq. (3.64) may be disregarded):

$$i \cong i_{*,ref} \left[\left(\frac{C_{H_2,bulk}}{C_{H_2,ref}} \right)^a \exp \left(\frac{\alpha_a \mathcal{F} z_{e,an} \eta_{A,an}^{bulk}}{\mathcal{R}T} \right) \right], \quad \text{with } \eta_{A,an}^{bulk} \gg \frac{\mathcal{R}T}{\alpha_c \mathcal{F} z_{e,an}} \quad (3.66)$$

when written in terms of the activation polarization, Eq. (3.66) becomes

$$\eta_{A,an}^{bulk} \cong \frac{\mathcal{R}T}{\alpha_a \mathcal{F} z_{e,an}} \ln \left[\frac{i}{i_{*,ref}} \left(\frac{C_{H_2,ref}}{C_{H_2,bulk}} \right)^a \right] \quad (3.67)$$

Note that it has been made explicit that the activation polarization is now referred to the bulk gas concentration, $\eta_{A,an}^{bulk}$. Combining the “Nernstian loss” ($\eta_{C,Nernst}$), as given by Eq. (3.60), and the “kinetic loss” ($\eta_{C,BV}$) in a general expression for the concentration polarization, one obtains

$$\eta_{C,Nernst,an} \cong \frac{\mathcal{R}T}{z_{e,an} \mathcal{F}} \ln \left(\frac{i_{L,an}}{i_{L,an} - i} \right) \quad (3.68)$$

$$\eta_{C,BV,an} = \eta_{A,an}^{TPB} - \eta_{A,an}^{bulk} \cong \frac{\mathcal{R}T}{\alpha_a \mathcal{F} z_{e,an}} \ln \left(\frac{i_{L,an}}{i_{L,an} - i} \right)^a \quad (3.69)$$

$$\begin{aligned} \eta_{C,an} &\cong \eta_{C,Nernst,an} + \eta_{C,BV,an} \cong \frac{\mathcal{R}T}{z_{e,an} \mathcal{F}} \left[\ln \left(\frac{i_{L,an}}{i_{L,an} - i} \right) + \frac{a}{\alpha_a} \ln \left(\frac{i_{L,an}}{i_{L,an} - i} \right) \right] \\ &\cong \frac{\mathcal{R}T}{z_{e,an} \mathcal{F}} \left(1 + \frac{a}{\alpha_a} \right) \ln \left(\frac{i_{L,an}}{i_{L,an} - i} \right) \end{aligned} \quad (3.70)$$

The application of Eq. (3.70) in lieu of Eq. (3.60) is of questionable usefulness, as the former relies in a very particular definition of concentration polarization which, as mentioned in the foregoing, is seldom invoked. The so-called “concentration-induced kinetic losses”, as defined by Eq. (3.69), might be seen as an indirect concentration loss, rather than the concentration polarization itself. Nonetheless, such “conceptual artificiality”, applied in order to distinguish between the conditions at the TPB from that of the bulk flow, could be of interest if one is concerned in “bookkeeping” several types of polarizations, based on somewhat discretionary criterion for identifying these very same polarizations (similar to what has been pointed out in **§§2.3**). What should be clear is that in using Eq. (3.67) and (3.70) one is actually “transferring the evaluation” of $\Delta\phi_{eq,an}^{tpb}$ from the term $\eta_{A,an}$ to $\eta_{C,an}$ (see also discussion in **§§2.3.4** and [143]). In other words, the effect of species concentration on potential steps, namely (note that the expressions below assume local equilibrium in the ionic phase of both anode and cathode^[144, 84, 102, 145]),

$$\Delta\phi_{eq,an}^{tpb} = (\phi_{an} - \phi_{elyt})_{eq} = \frac{1}{z_{e,an} \mathcal{F}} (\mu_{H_2O} - \mu_{H_2} - \mu_{O_2^\times})_{tpb} \quad , \text{ in the anode} \quad (3.71)$$

$$\Delta\phi_{eq,ca}^{tpb} = (\phi_{ca} - \phi_{elyt})_{eq} = \frac{1}{z_{e,ca} \mathcal{F}} (2\mu_{O_2^\times} - \mu_{O_2})_{tpb} \quad , \text{ in the cathode} \quad (3.72)$$

Have been now taken into account through modified expressions for $\eta_{C,an}$ and $\eta_{C,ca}$, respectively, akin to the formula given by Eq. (3.70) in the case of anode. Thus, in this particular case, the voltage losses $\eta_{C,an}$ and $\eta_{C,ca}$ do not constitute pure concentration polarizations in the “Nernstian sense”, but a “hybrid polarization” that also incorporates indirect losses ($\eta_{C,BV}$) associated to electrode kinetics, caused by changes in species concentration.

The usage of Eq. (3.70) can become difficult to work with, if the corresponding phenomenological description of electrode kinetics is rather complex. For example, expressions for the exchange current density $i_{0,ref}$ (or, equivalently, i_0^V) are also themselves functions of species concentration^[83, 146, 84, 75, 121], as seen in **§§2.3.4**. Particularly, the

dependence of $i_{0,ref}$ on the surface coverage of oxide-ions ($\Theta_{O_{ad}^{2-}}$) might also be explicitly considered^[111, 116, 75, 121], thereby constituting another potential source of concentration-induced kinetic losses. However, this type of dependence is usually not described in a simple mathematical form that would benefit the formalism (and usefulness) of Eq. (3.70). Take, for instance, the following expression for the exchange current density of a MIEC electrode^[111]:

$$i_{0,ref} = 4 e k_{0,rev} K_{O_{ad}^{2-}} p^{1/2} \exp\left(\frac{2\mathcal{F}\Delta\phi_s}{RT}\right), \quad \text{with } \phi_s = \phi_s(\Theta_{O_{ad}^{2-}}, \dots) \quad (3.73)$$

where $k_{0,rev}$ is the rate constant (evaluated at equilibrium conditions) of the reverse reaction, e.g. Eq. (3.24a), which is also admitted to be the rate-limiting step in the case of this equation. To derive an expression in the form of Eq. (3.64) using the result of Eq. (3.73), so to obtain a formula as directed by Eq. (3.70), is not quite straightforward. More importantly, the merits of such derivation are not obvious on their own.

3.6 Brief Digressions on Mass Transport and Cross-Effects

The intent of this section is not put forth actual arguments to prove or disprove likely cross-effects, but to furnish a few brief remarks, which apparently departure from the main subject of this dissertation (*i.e.*, they are in fact brief digressions), that could illustrate what one really refers to when one discusses the relation between mass transport and cross-effects. In discussing cross-effects that stem from concurrent transport phenomena and how they can (or cannot) determine single-cell performance, the aim is to go beyond the topics frequently covered by the literature about mass transport in SOFCs. Usually, these cross-effects are either tacitly assumed to be negligible or the knowledge of their existence is just ignored. In the rare occasions when some of these cross-effects are evaluated, the applied phenomenological theory is, more often than not, misconceived^[59, 147, 148, 149, 150, 151, 152, 153].

The term “cross-effects” is a designation employed here to express the complex interaction between multiscale-multiphysics processes. The manifestation of cross-effects has many facets. For instance, they can manifest when physicochemical processes taking place on dissimilar spatio-temporal scales become somehow “linked” (or coupled) through the so-called “bridging scales”^[154, 155]. That is, these processes can start to interact once their characteristic scales “overlap” (*i.e.*, when they are within the same finite scale limit) and the constraints limiting their ability to influence each other are somewhat “weakened”. Here, particularly, the concept of “bridging scales” is inserted in the context of developing accurate large scale descriptions of particles interacting in the small scale^[156], especially when microscopic interactions emerge on a large scale and the specific (“unaveraged”) details from their

microworld affect the validity of macroscale deterministic field equations. Very crudely this is to say that the hydrodynamic behavior of microscopic systems non-longer has an infinite scale separation^[156, 157, 158].

Since a proper description of “microscale-to-macroscale interactions” depends on specific mathematical models, cross-effects may be seen as the physical manifestation of the many possible mathematical couplings that are allowed to occur as a coupled effect of irreversible processes, under certain conditions, according to an established theoretical framework. Among the existing frameworks, the one proposed by the thermodynamics of irreversible processes⁸ (TIP)^[79, 80, 159, 160, 161] seems to provide the most intelligible (and numerous) examples in the mass transfer literature. Moreover, engineers (specially chemical engineers) are usually acquainted with TIP, as it forms the cornerstone of the so-called linear phenomenological transport theory, or just “transport phenomena theory”^[162, 163]. Presumably, the most common examples of cross-effects (or “reciprocal phenomena”, in the usual terminology used by TIP) between irreversible processes are^[45, 164]: (i) coupling of heat and mass diffusive transports, namely Soret-Dufour effects; (ii) thermoelectric phenomena, namely Peltier–Seebeck–Thomson effects; (iii) electrokinetic (and mechano-electric) effects; (iv) and the lesser-known, “chemical viscosity”^[165].

However, the results from this specific continuum theory ought not to be used in drawing definitive conclusions about what cross-effects are or whether they can or cannot occur (e.g., see debate on the illusive “Curie principle”^[148, 150, 151]). First and foremost, one would need to start with more “conceptually robust” frameworks, such as rational thermodynamics, extended non-equilibrium theories, mesoscopic hydrodynamics, and the like^[150, 166]. This is indeed the case when “cross-effects” are to be generalized to include additional cross-relations between driving forces, property fluxes, and constraining surfaces; relations that are not considered by classical theories of transport phenomena (e.g., see [167]). On the other hand, “extended frameworks” often require intricate mathematical developments and vigorous diligence in order to perceive the abstract mathematics inherent to these more advanced theories. For this reason, TIP is usually employed with the intent of constructing simplified expositions.

In any event, it is important to have in mind the intrinsic limitations and the possible inconsistencies of applying the linear theory of transport phenomena (unfortunately, however, this is seldom the case in the literature). The ordinary case is that these limitations are only discussed when the possible shortcomings of the local equilibrium hypothesis^[79] (or postulate) are brought about. The “violation” or inadequacy of this theoretical assumption is quite often

⁸ Also referred to as linear non-equilibrium thermodynamics or classical non-equilibrium thermodynamics.

justified only for systems “far-from-equilibrium”^[168]. Even though this is surely true, it remains to be properly defined what is the “far-from-equilibrium physics” one is specifically talking about. Concerning this aspect, the analysis of “equilibrium versus non-equilibrium” states in non-condensed matter seems to be restricted to the evaluation of the relative importance of local gradients in state variables^[169, 170]. Thus, emphasis is only placed on the gradient magnitude itself and not on the effects related to transport processes “competing” on disparate physical scales, the latter case being (often) overlooked. This is to say that it is not solely the magnitude of local gradients that should be taken into consideration when evaluating cross-effects, but also the comparative importance (e.g., ratio) between gradients of different state variables and how these are correlated over their characteristic length and time scales. Furthermore, failure to recognize the correct number of degrees of freedom in the “microscopic” thermodynamic description can lead to a subtle violation of the “local equilibrium” postulate, which lies in the core of TIP theory.

As it has been stated above, the validity of phenomenological macroscale equations can be compromised when the large scale description, provided by these equations, is controlled by the details of microscopic interactions. In practice, however, many times all that one can observe are changes in the macroscopic state described by gas quantities (e.g., density, velocity, temperature, stresses, and heat flux) that are (supposedly) related to suitable averages of quantities depending on microscopic states^[171]. From this point of view, one needs to establish certain hypotheses regarding the structure and interaction of molecules, for which the precise details are rarely known unless for only oversimplified systems. At this point, one faces a great difficulty that affects not only the TIP framework, but virtually any macroscale-continuum phenomenological approach (e.g., see [172]): “to explain things that are seen and directly measurable by means of imagined things that are not seen and not directly measurable”^[171]. Based on these established hypotheses, one needs to ascertain whether measurable macroscopic quantities do or do not approximate the *a priori* assumed relations between those macroscopic gas quantities. It seems apparent that the imperfect representation of the actual molecular behavior by “model molecules” or “fictitious particles”^[171, 77] might impair any successful undertaking. The odds of getting plausible results are further minimized when there is the necessity of considering only the description of ideal systems, in contrast to more realistic situations wherein definitions such as the mean free path, for example, can lose some of their definiteness if the molecules are surrounded by “non-idealized” force fields^[173, 174]. On the other hand, the modeling complexity might be enormously magnified if some of these simplifying conditions (e.g., absence of force fields) are relaxed to the detriment of a realistic description.

In the traditional approach it is usual to begin with the necessary governing equations⁹ and a set of general constitutive equations (sometimes also referred to as “rate equations”) based on the principles (and accepted hypotheses) from TIP. In the context of TIP, rate equations are flux relations needed in order to relate mass, momentum, and energy fluxes. On this particular aspect, many existing mathematical models utterly fail, insofar they “are unable” to recognize the coupling between additional fluxes and thermodynamic driving forces, beyond those dictated by the existing state of affairs in mass transfer theories, such as the “Curie Principle”^[80, 159, 162]. Extended non-equilibrium theories show^[150, 149, 175, 176], however, that the property expressed by the “Curie principle” follows from pure tensorial (isomorphism) arguments, *i.e.* from the isotropy of linear constitutive functions and from the representation theorems of such functions^[177, 178]. On the other hand, theorems for nonlinear isotropic constitutive functions (*e.g.*, see [179, 180]) show that this “principle” is not valid in general. Thus, in spite of many TIP advocates have been contumaciously defending the “Curie principle” using mostly rhetorical arguments^[181, 162, 65, 64], it must not be considered a comprehensive physically-based restriction.

More specifically, and what is of most interest in this dissertation work, the phenomenological modeling of mass diffusion in multicomponent fluid systems^[182, 183, 184, 64, 185, 186, 187, 188] has also been littered by this theoretical myopia originated from the “Curie principle” stigma, even in the cases where the model was originally derived using the results of kinetic theory or based on statistical mechanics considerations. In addition, it is not uncommon to have errors in the derivation of transport equations that are really hard to grasp, because they arise from subtle inconsistencies when one tries to translate “concepts from the microworld” to the large scale description. This is the case of [188], wherein an erroneous formulation of the interspecies “diffusion kinetic energy”^[60, 189] leads to misleading assertions about the “what is correct expression” of the chemical potential, when formulated as the driving force for mass diffusion processes. There are exceptions, certainly, or at least there are partial exceptions, where consistent mathematical models were indeed derived based on a phenomenological description of hydrodynamic diffusion, but these works (*e.g.*, see [190, 191, 192]) have been either obscured over the years or have not attracted enough attention from scholars in both the chemical engineering and SOFC research communities. Still in the context of mass diffusion, examples of cross-effects that have been commonly overlooked by unfavorable analyzes, biased by the views of TIP, include: (i) diffusion slip^[193, 194, 195, 196, 197, 198, 199] phenomenon¹⁰; (ii)

⁹ Governing equations are usually referred to as “conservation laws”, although a better terminology would be “balance laws” as some of these equations are not really, strictly speaking, statements of conserved quantities (such as in the case of the specific entropy^[78]).

¹⁰ Also referred to as the “Kramers-Kistemaker effect”.

barodiffusion^[200, 195, 201], and (iii) shear-Induced migration^[202] (non-equilibrium “diffusion-like” movement of mass, which is influenced by the presence of walls, as in the case of rarefied gas flows in porous media^[203, 204, 153, 205]).

Modern installments of classical textbooks on mass transfer, such as the works of Bird *et al.*^[162], Deen^[206], and Slattery^[207], still relies on a faulty understanding of multicomponent mass diffusion, by disregarding “non-conventional” cross-effects and (as will be addressed in the next paragraphs) also the effects of chemical reactions on diffusive transport, momentum closure, and the ratio of total mass fluxes. Furthermore, the Curie principle is again invoked to state that diffusion flux, chemical reactions, and momentum do not interact whatsoever, even though there is empirical evidence proving otherwise^[202, 208, 165]. It is interesting to note, however, that Landau and Lifshitz^[209], in their famous and respected “Course of Theoretical Physics”, have made an important comment that goes beyond their typical TIP-based derivation for the equations of fluid dynamics. They recognized that (based on kinetic theory arguments) the high-order derivatives of momentum quantities, such as the Laplacian of the velocity field, may couple with the diffusion density vector (*i.e.*, mass flux), depending on the order of magnitude of certain characteristic length scales that govern the rate of momentum transfer. Here Landau and Lifshitz were referring to the barodiffusion effect, as conceived by Zhdanov and coauthors^[200].

To conclude the present section, another matter of great controversy, now concerning the ratios between species fluxes, is presented. Although many works in the literature discuss a physically motivated origin for the ratio of the total mass (or molar) fluxes^[210, 59, 211, 212, 213, 214, 197, 215, 216], this is not a completely solved issue and it remains, to a great extent, a zone of theoretical uncertainty. Equimolar counter-diffusion, Graham’s Law, and flux ratios defined by chemical reaction stoichiometry are among the various alleged flux “constraints”. Nevertheless, one must note that in the absence of chemical reactions the ratio of fluxes is beyond any “predetermined control” and flux ratios must adjust themselves to satisfy the balance law of momentum (for both the mean motion and for each species contained in the gas mixture). At this point resides an additional problem related to the (*a priori* unknown) nature of the constitutive equations that should be incorporated into this balance law. Distinct transport mechanisms in Knudsen, viscous flow, and transition regions^[210] seem to greatly difficult this task of ascertaining the correct use of material-dependent constitutive information. Finally, added to this is the fact that total fluxes might not be correctly (unambiguously) expressed relative to any frame of reference^[217, 218, 219, 211, 220, 221, 222, 223], as in the case of mechanically constrained porous membranes.

The drag of the moving species on the porous matrix will tend to move the membrane, unless it is mechanically constrained (*i.e.*, unless the interphase “hydraulic” drag is counter-reacted in some way). Assuming the porous matrix as a “non-deformable solid”, it will transfer the contact (frictional) forces to the support that ties the matrix to its surroundings. Thus, in order to the membrane remain stationary an external “clamping” force exerted by the supports on the membrane must be applied. As a result of this force that prevents membrane movement, there can be pressure gradients whether or not there are body forces in the fluid system. By their turn, these pressure gradients (or other external “unbalanced forces” acting on the permeating gases) may cause viscous flow based on purely hydrodynamics considerations. Even though one can identify a “viscous velocity” for the mean flow (*i.e.*, mixture’s mass-average velocity), it may not be the situation for the individual viscous velocities of the components, which are about the same only if there are no additional forces hindering their movement relative to the fixed frame of reference (*e.g.*, adsorption forces on pore walls). It comes without saying that in this case the gas-matrix (*i.e.*, gas-wall) friction terms (“Knudsen diffusivities”) will determine the ratio of fluxes.

However, in the presence of chemical reactions (occurring in the bulk volume and/or on the surfaces of solid obstacles) the momentum balance equations do not suffice to determine the flux ratio and supplementary information is therefore necessary, many times in the form of second law thermodynamic constrained inequalities, such as those derived from the linear non-equilibrium thermodynamics formalism^[80, 79] (*e.g.*, binomial combinations of “thermodynamics forces” and conjugated fluxes or transport rates). When chemical reaction occurs within a porous domain, is the flux ratio is determined by the stoichiometry of the reaction? Since the flux ratio determined by the stoichiometry may differ from the flux ratio required to satisfy the momentum governing equation at uniform pressure, internal pressure gradients may accompany chemical reactions, as suggested by Hoogschagen^[214] and Haynes^[212]. One can suspect that these gradients to be significant whenever chemical reactions rates are sufficiently intense (*i.e.*, resulting in “large” spatial gradients in the mean gas density) and if pore diameter is sufficiently small (*i.e.*, resulting in appreciable rarefaction effects). More precisely, if a chemical reaction (or a set of reactions) causes a net change in the total number of moles, then it will cause a pressure gradient. In fact, this change will result in a net molar flow of gas into (or out) the domain and the pressure will be higher (or lower) inside the domain than outside. Nonetheless, additional research is required to elucidate the factors which determine the flux ratio in these cases. Be that as it may, the effects of internal pressure gradients in the porous SOFCs layers are often neglected. However, neglecting pressure gradients leads to inconsistencies in the flux calculations^[224, 225] and it can certainly

violate mass conservation, sometimes in a very obvious manner (e.g., when mass fractions do not add up to unity^[66]).

In the general case, the species conservation equation and constitutive equations for mass diffusion flux (e.g., Maxwell-Stefan equation) must be supplemented by an equation for the macroscopic pressure gradient in the system. The simplest (and usual) approach in the SOFC literature is to consider the total pressure constant (as will be seen in **Chapter 4**). However, as pointed out above, this alternative is inadequate if species concentrations are non-uniform along the system. When it is considered, the establishment of a pressure gradient in the system is usually linked through the local Gibbs-Duhem equation (GDE):

$$\nabla p = \sum_{k=1}^{N_{gas}} C_k \left(\sum_{j=1}^{N_{gas}-1} \frac{\partial \mu_k}{\partial y_j} \nabla y_j \right) = \sum_{k=1}^{N_{gas}} C_k \left(\sum_{j=1}^{N_{gas}-1} \frac{\partial \mu_k}{\partial y_j} \nabla_T y_j + \frac{\partial \mu_k}{\partial T} \nabla T \right) \quad (3.74)$$

where $\mu_k = \mu_k(T, p, y_1, y_2, \dots, y_{N_{gas}-1})$, which thereby eliminates degrees of freedom of the system. That is, under the assumption of thermodynamic equilibrium and phase homogeneity, the GDE places a restriction on the simultaneous variations in the intensive thermodynamic variables of a given multicomponent phase. In principle, nevertheless, the GDE as expressed above applies only to homogeneous macroscopic systems. For instance, the GDE does not remain valid for systems having internal state variables^[151], inhomogeneous (*i.e.*, as in nonadditive) entropies^[226, 227], or long-range interactions^[228] such as those giving rise to shear viscosity.

Rigorously speaking, therefore, the GDE alone should not be used for deriving conclusions about the pressure gradient of non-equilibrium flows in porous bodies^[229]. Even if the GDE is valid under the assumption of local equilibrium, the pressure term that appears in this equation cannot be unambiguously identified with the macroscopic pressure gradient from the momentum (“hydrodynamic”) balance equation. Instead, it compares with a local gradient that is only valid (*i.e.*, properly defined) within the considered infinitesimal finite-volume. Similar criticism has been already suggested by Truesdell^[230] for multicomponent diffusion theories based on TIP.

The ambiguity concerning the use of GDE in the TIP formalism dates back to the work of Prigogine^[159], more specifically “Prigogine’s theorem on the independence of the (entropic) dissipation function on the choice of reference velocity”, a result that was further noted by Lightfoot^[163]. In this particular context, the GDE has been used “to prove” that the summation of so-called “diffusion driving force” over all mixture components is identically zero in all domain interior points. Krishna and other authors^[64, 65, 185, 65, 231, 232], in their derivations of Maxwell-Stefan equations, have also implicitly assumed that the pressure gradient as defined

by GDE is valid in the condition of “mechanical equilibrium”, that is, when the sum of pressure-driven forces and body forces acting on the fluid per unity mass (or volume) is vanishing small¹¹. These controversial derivations also convey ambiguity and can result in misleading conclusions about the validity of Maxwell-Stefan equations. Moreover, in the presence of external forces (such as those stemming from the mechanical restraint a membrane) the entropic dissipation function depends explicitly on the mass-average (center-of-mass) velocity and thus the reference velocity for diffusive fluxes cannot be chosen arbitrarily, making Prigogine's theorem invalid^[219, 217 229].

The short essay that has been presented in the preceding pages, besides expressing the author's academic opinion on the phenomenological modeling of mass diffusion in multicomponent fluid systems, is so provided to put into perspective the content of **Chapter 4** (specially the models representing the diffusive mass transfer within porous SOFC layers). As none of the topics analyzed and evaluated in the present section will be covered in the remaining parts of this work, with the exception of what is examined in **§§A.5** (see **APPENDIX A**), it is important to make the following clarifications:

- I. Most (if not all) mass transfer models in **Chapter 4** are theoretically flawed in their very core. Nevertheless, they may be (and, in fact, they are) still successfully used in the numerical simulation of SOFC devices, but solely based on their verifiable empirical consequences. Thus, “errors” and limitations mentioned in this section do not, in general, invalidate these phenomenological models from a pragmatic standpoint.
- II. However, even though these mass transfer models have been “safely” applied in the simulation of solid-oxide fuel cells, in what conditions these models can in fact be used remains a problematic and critical issue. That is, it remains unclear what their applicability limits are and so remain their trust-regions, whose knowledge is necessary to establish confidence in the results of numerical simulations.

¹¹ It is worth noting that shear stresses terms have not appeared during their derivations and no reasons were provided for such omission.

Chapter 4

MODELING TECHNIQUES IN CONCENTRATION POLARIZATION

4.1 Introduction

In general terms, modeling techniques aim to obtain some sort of representation, usually of mathematical form, of the state of a natural system. The result of mathematical modeling is the description of multiphysics processes (*i.e.*, a description about how the natural world is believed to function) using a set of concise mathematical concepts and rules. It is hoped that the model may help to explain and also make “predictions” about the behavior of the natural system, especially when studying the effect of changes in influential factors or components of this system.

Mathematical modeling can be utilized as either a theoretical or working tool^[233]. The latter is mostly concerned with quantitative models (usually to support some kind of decision making), while the former is more comprehensive in scope, also including process qualitative aspects. Qualitative aspects are central, for example, when one is interested in developing a scientific understanding of the intricacies of multiphysics processes, rather than to only accurately quantify them. There is a wide spectrum of modeling techniques, thus aprioristic classification of all these techniques, in pre-determined groups, is to some extent subjective and views about such classification may differ amongst different authors^[234]. In this work, notably, a simple classification is proposed (see Fig. 4.1) to highlight the goal of a given mathematical model. This classification involves the so-called “white-box” and “black-box” models, so referred to as “physical modeling” and “empirical modeling”, respectively.

Figure 4.1: classification of the mathematical models discussed in §§4.2 through §§4.8 (figure by the author).

Models are classified as white-box when the state of the system is accurately known and its behavior can be described in the form of “balance laws” (equations of mass, momentum, and energy conservation) and “constitutive equations” (equations involving material properties). These models, allegedly, often lead to the most general description of multiphysics processes. However, there are critical elements of compromise in such modeling approach. The majority of natural systems are far too complicated to model in their entirety, thus in practice white-box models demand comprehensive interdisciplinary scientific research, often resulting in very complex mathematical descriptions. Therefore, when applying white-box models, the first kind of compromise is to identify the most relevant parts of the system that will be included in the model and what will be wisely disregarded. The second kind of compromise concerns the amount of mathematical manipulation (computation) which is feasible under certain established criteria (e.g., simulation runtime, computer memory usage, and so on). Although physically-based models have the potential to provide more general results, these results do not come without additional costs, such as the development of more robust, reliable, and complex numerical methods.

Models are classified as “black-box” when the state of a system is not known and its behavior is described through a collection of input data (“what influences the system behavior”) and output data (“the resulting behavior of the system”). Historical data are used to develop models that can describe the dependencies between input and output data. Data sets usually constitute empirical information, but it may not always be the case (e.g., part of the data could be obtained with help from physical modeling). In this sense, black-box models departures from the purely theoretical description of a process. Black-box models are frequently used as the basis for predictive control and dynamic optimization of industrial-scale systems due to their relatively cheap computation effort and simple mathematical structures, which are used to solve the problem in question (*i.e.*, processing inputs and predicting outputs).

The goal of the present work is to analyze physical modeling techniques. Thus, reviews about black-box models will be touched on very briefly. By the expression “typical modeling techniques” it is meant the most representative (white-box) models applied in the SOFC literature. Certainly it would be impossible to include all modeling techniques presented to date, and this would be a meaningless task as well, given that the content of this dissertation will inevitable age from the moment it is published. The following critical review should help drawing some general ideas about what delineates the fine lines separating judicious simplifications (when the most relevant parts of the system are correctly identified) from “theoretical fantasies” (when such identification is misleading).

4.2 System-Level Models: Univariate and Multivariate Modeling

Traditional SOFC models proved of little use for power plant modeling^[235], mainly because most of the effort has been devoted to depict the intricacies of primordial microscale electrochemical processes that occur on electrode surfaces. Thus, significantly less attention was directed to the development of system-level models. Furthermore, traditional models often reveal themselves overly sensitive to minute changes in parameters, which makes them unsuitable for distinguishing between “design point” and “off-design” operation of specific plant components, hindering the overall process of system optimization^[235]. From the engineering point of view, when developing models for power plant modeling purposes, the critical requirement is to have a mathematical model which gives reasonable results, and can be used, with the required confidence level, for design and device selection purposes. Phenomena occurring on electrode surfaces, although important, must not take up an inordinate amount of attention^[235]. Moreover, these small scale phenomena are difficult to

measure and, as a result of this, large sets of experimental data are seldom available. For industrial-scale systems, however, a mathematical model is worth little without reliable validation and thus hard experimental data are mandatory. “Hard data” are those whose experiment offers both a complete narrative about experimental procedures and detailed information on operating parameters. Especially for fully-empirical black-box models, the lack of reliable data undermines any serious attempt of validation.

System-level models represent a significant simplification when compared to more complex physically-based modeling approaches. Their simplicity comes from the fact that they can use simpler “processing rules” (applied to a large collection of data sets). Another advantage of these system-level (black-box) models is that they can create functional relations between inputs and outputs solely on the basis of experimental data, ignoring phenomenological approaches. Therefore, fully-empirical models can be implemented in those cases where physical models are inexistent or are unfeasible for practical reasons. A notorious drawback is that fully-empirical models are able to “detect” only those dependencies that are already present in the data used to develop the processing rules, thus precluding any general description of such dependencies^[235]. To tackle this problem, at least partially, one can combine modeling through “first-principles” and data-based approaches^[44]. There are a number of works in the SOFC literature that applied pure (data-based) black-box models, or a combination of these with *ad hoc* physical modeling techniques, to support analysis at the system level. In these works, the system under study considered either only the fuel cell stack or the entire SOFC module, which further included BOP components (e.g., anode recycle plenum; pre-reformer; ejectors; compressors; turbines; and heat exchangers). These system-level models have been most often used to: (i) optimize SOFC designs under steady-state conditions; (ii) estimate SOFC state during transient operation, *i.e.*, track the profile of operating variables during step changes in the cell current density, or in other input parameters; and (iii) dynamic modeling for predictive control purposes. In this context, some selected works of the literature will now be briefly reviewed.

Milewski and coworkers^[235, 236] applied the artificial neural network (ANN) model to simulate the SOFC parametric behavior, merely utilizing available experimental data (*i.e.*, in this case the ANN was implemented as a fully-empirical model). Potentially, analyses based on the results obtained could then be used to optimize the SOFC design. However, in this work the objective was only to analyze the effects of various (operating and design) parameters, such as: fuel flow; fuel utilization factor; diluents types and their concentration; oxidant flow; oxidant utilization factor; and cell operating temperature. The testing apparatus was a single planar stack installed in a heated ceramic furnace. The investigated cell was a circular type

seal-less SOFC ($NiO/8YSZ$ cermet anode). The ANN model^[237, 238] is based on the so-called methods of artificial intelligence (AI) that, in rough terms, try to imitate the methods of data processing of living organisms in order to describe phenomena of interest^[239]. The application of AI methods to solve engineering and scientific problems is a result of the emergence of a new research field called “empirical modeling and data mining”, which brings together computational intelligence, statistics, and numerical methods. This field is also referred to as “soft-computing”^[240, 241]. The model developed by Milewski and coworkers to simulate a SOFC provides an alternative to overcome the limitations of simple linear physical models, which do not enable accurate quantitative description (although they can qualitatively capture the main features) of highly nonlinear physical phenomena. Such limitations are more acute when the system under analysis has multiple inputs (parameters and/or variables), as in Fig. 4.2. Even though ANN models use computationally simple methods to build dependencies between inputs and outputs, they have good nonlinear properties and thus are capable of identifying possible solutions with relative easiness, when compared to physical modeling approaches (for system-level problems, at least).

Figure 4.2: ANN is an interconnected group of nodes, akin to the vast network of neurons, which mimics the behavior of human brain. (a) Here, each circular node represents an artificial neuron and an arrow represents a connection from the output of one neuron to the input of another; (b) input parameters of an ANN-SOFC model; (c) hybrid ANN model, where constitutive equations are applied for the ionic conductivity of solid-oxide electrolytes (figure by the author).

A hybrid model was also implemented by Milewski *et al.*^[235], consisting of an ANN model and mathematical expressions (phenomenological models) for some input parameters (see Fig. 4.2c). Through this model, Milewski and coworkers investigated various input parameters, one by one, and one of these models was created with 12 input parameters and one output (see Fig. 4.2c). One may refer to the latter case as univariate modeling in respect to outputs. These authors utilized 31 voltage-current curves (comprising over 580 experimental points) to train a network wherein the cell voltage was the only output parameter. The network was trained until it learned the experimental data within a maximum acceptable error level. Note that large data sets are required for both ANN training and final model validation.

Available experimental data can teach ANNs about the global effect regarding certain parameters that impose concentration losses to a SOFC, such as anode porosity and fuel dilution (see Fig. 4.3). However, ANN models are unable to provide any direct discrimination of associated voltage drops that are related to this or that type of polarization, among which is the concentration polarization. The process's phenomenology is “hidden” by processing rules, which are, by their turn, built within the various neuron layers. In other words, cause-effect relations are not unambiguous, even when evaluating one parameter at time. Thus, at first, conventional ANN models are not suited to study the inner structures of multiphysics processes. This is not a problem, if one applies black-box models considering the objectives already set out above for system-level models. ANN models can also be used to “extend the range of experimental results” and additional data so obtained could be used as a reference for comparison by physical modeling approaches. Obviously though, this procedure should not be taken as equivalent to any true validation test.

Figure 4.3: (a) anode porosity dependence modeled by ANN; (b) result of ANN simulation training data of H_2/N_2 (at constant flow rate) showing fuel composition dependence^[235]. Note inaccurate results for the extrapolated case of 0% of H_2 (the network gives nonphysical results, *i.e.* SOFC generates electrical current with no fuel being delivered).

Other types of data-based modes have been developed for SOFCs. Firstly, there are those which are combined with *ad hoc* physical models and thus take into consideration more details of chemical and thermal aspects, requiring the solution of a set of nonlinear ODEs^[242, 243, 244]. In the most common situation, these physics-based models are zero-dimensional or quasi-1D models of fuel cell system components^[245, 246, 247, 248]. Secondly, there are dynamic models that are mostly data-based and developed through a system identification approach^[44, 249]. These data-based dynamic models can be used to investigate responses of SOFCs under different operating conditions and then, by means of optimum control, one can steer the operating conditions towards a more favorable operating point (“off-design” condition), so to improve durability and efficiency of fuel cells^[44]. Process modeling, state estimation, and design of the controller itself are part of advanced processes control strategies. They are intrinsically dependent on each other, insofar as the model development affects both the design of the controller and selection of state estimation techniques. In general, data-based modes are most useful for controller design purposes. Both advanced controls (e.g., nonlinear model predictive controller) and conventional controls have been implemented in SOFC power systems.

There is no point in discussing data-based models any further, as this would not benefit the main goal of this work. Nonetheless, one final remark can be made about physics-based model-predictive control of SOFCs. The key point of these models is that they try to incorporate physical knowledge about SOFC behavior into real-time MIMO (multiple-input and multiple-output) process-control strategies. More precisely, the controller includes some (reduced) form of a “high-fidelity”, physics-based model that represents physical-chemical processes. However, because such complex nonlinear model cannot be solved in real time, as part of the controller logic, linear reduced-order state-space models are required. The model reduction is accomplished via system identification, which is the data-based part of the modeling technique. Before this reduction step, one needs to first select a simplified (“lumped”) physical model to describe the mass diffusion of gas-phase species. The next step consists in deriving a transfer function (Laplace transform) of the chosen mass transport equation and then to incorporate it into the set of time-dependent ODEs that represent the overall mass balance, which is written in a format suitable for process control purposes (*i.e.*, a model which approximates derivatives of input variables from measurable variables). Ultimately, the objective is to design controller input signals in terms of the partial pressures of gas-phase species^[250], as exemplified on Fig. 4.4. Thus, physics-based model-predictive control is more about the method of deriving state functions and establishing a control strategy, and much less about the fidelity of physical models.

other hand, analytical solutions resulting from a suitable (carefully chosen) model can show the explicit parametric dependency, a “general behavior” that can be inferred from closed-form mathematical expressions. Because these solutions offer a transparent view into how variables/parameters and interactions between variables/parameters affect the result, they may significantly facilitate the understanding of SOFC processes. Furthermore, sometimes they can even predict novel effects affecting cell performance^[251, 252] or can be used to pinpoint inconsistent results of a specific mathematical model^[253].

The models in this section are based on similar considerations as those of the models that will be reviewed in §§4.5: considerations that stem from a macro-homogeneous approach. However, mathematical models in §§4.5 are “mathematically more complex”, and for this reason they will almost invariably require numerical solutions. More importantly, they do not share the same specific goals of analytical models. Although this will be further explored in the next section, a few words about the macro-homogeneous approach may be instructive before proceeding to the discussion of analytical models. This approach, roughly speaking, “ignores” the microscopic details of SOFC porous layers, which are now considered as a “new continuum” (*i.e.*, as an “interpenetrating continuum media”) with “homogenized” or lumped properties, which are usually taken from experiments or from microstructural models. Even though the macro-homogeneous approach has no convincing physical justification (it is a mathematical construct, after all), theoretical results obtained through this approach, within certain restrictions, have been validated by experimental data with reasonable agreement between them. Nonetheless, it does have limitations and they are plentiful, as will be examined more closely in this chapter.

4.3.1 Kulikovsky’s Model for the Active Layer

The main features of the active layer of a SOFC have been already succinctly described in in §2.3.3. Here a simplified mathematical model for this layer is presented, which investigates the effects of mass-transport on an electrochemical reaction obeying either Tafel or Butler-Volmer kinetics. To this end, the model of Perry–Newman–Cairns^[104] was generalized by Kulikovsky^[12, 107] to investigate the active layer (see Fig. 2.10) of an generic electrode (anode or cathode), considering the situations of ideal ionic transport and/or ideal gas mass transport. Kulikovsky has also incorporated further simplifications to contrast a number of limiting cases that are encountered at high or low current density regimes. Despite these simplifications (some of them are clearly unrealistic for real SOFCs), this model gives a reasonable account of the qualitative aspects of the problem, without inordinate mathematical complications.

In the specific case of Kulikovsky's analytical models, a more detailed examination was given in this dissertation (see **APPENDIX A**) not because these models strictly fit the objectives of the present work, but because their analytical nature allow pinpointing, in a clear and general way, the definitions of “activation polarization” and “augmented polarization” (as already examined in §§2.3.1-§§2.3.4). However, the lengthier discussion was left to the appendix section to maintain the argumentation flow of this chapter leaner. By way of example of what ought to be criticized, Kulikovsky considers simplifying assumptions that do not hold for SOFCs, such as disregarding (as a general case) the importance of steam in anode kinetics. Kulikovsky tries to substantiate this assumption by citing one very specific reference^[254] and then claiming that “the modeling study indicates that the water concentration dependence is weak and to a first approximation it can be ignored” (see [255], pp. 6687). Although simplifications such as this may well fit the goals of an analytical model (of qualitative, almost didactical character), the argumentative strategy seems fallacious because that author tries to bestow upon the model a greater generality than can be justified based on its original premises or beyond over-simplistic arguments (unreasonable assumptions). Surely one can treat complex problems as if they were much simpler than they really are, but the limitations and “pitfalls” of such simplified treatment must be duly informed. Modeling generalizations are undoubtedly of great value, but they come at a “cost” and what “cost” this is should be assessed with fair-mindedness.

Kulikovsky derived analytical models for the particular cases of ideal ionic transport and ideal gas transport, and for each of these cases the limiting situations of high and low current density were considered for further simplifications. Kulikovsky starts with the following system of equations, which governs the active layer performance (see **APPENDIX A**):

$$\frac{\partial i_{io}(z)}{\partial z} = -i_*^{\vee} (C_{fg}/C_{ref})^{\alpha} [\exp(\eta/b_{ts}) - \exp(-\eta/b_{ts})] = -2 i_*^{\vee} (C_{fg}/C_{ref})^{\alpha} \sinh(\eta/b_{ts}) \quad (4.1)$$

$$i_{io} = -\sigma_{io} \frac{\partial \eta(z)}{\partial z} \quad (4.2)$$

$$D \frac{\partial C_{fg}(z)}{\partial z} = \frac{i - i_{io}}{z_e \mathcal{F}} \quad (4.3)$$

where z is the coordinate along the active layer thickness (on Fig. 2.10 it is directed from the electrolyte to the anode outer layer); $i_*^{\vee}$ is the volumetric exchange current density; C_{ref} is a reference molar concentration of feed gas; α is the reaction order in respect to feed gas; η is the half-cell (e.g., anodic) augmented polarization; σ_{io} is the effective conductivity of electrolyte phase in the active layer; D is the effective diffusion coefficient of feed gas within the porous channels of active layer; α is the charge transfer coefficient; and b_{ts} is the Tafel slope.

According to Kulikovsky, Eq. (4.1) expresses the decay of ionic current with z at a rate given by Butler–Volmer electrode kinetics (RHS of this equation); Eq. (4.2) states that Ohm's law is valid for the electrolyte phase, relating the ionic current to the overvoltage gradient; it is a material balance that establishes that the local diffusion flux of feed gas is equal to the local electronic current density ($i_e = i - i_{io}$) to be converted through the half-cell electrochemical reaction (molar flux of ions to be converted into free electrons); and the stoichiometry factor $z_e \mathcal{F}$ in Eq. (4.3) does the conversion of current density to molar flux. In order to solve the problem, Kulikovsky nondimensionalized Eq. (4.1), (4.2), and (4.3) by using the following dimensionless variables and characteristic scaling parameters:

$$\hat{z} = \frac{z}{l_t}, \quad \hat{\eta} = \frac{\eta}{b_{ts}}, \quad \hat{C} = \frac{C_{fg}}{C_t}, \quad \hat{i}_{io} = \frac{i_{io} l_t}{\sigma_{io} b_{ts}} \quad (4.4)$$

where C_t is the feed gas concentration at the active layer/outlet layer interface ($z/l_t = 1$, as per Fig. 2.10). The subscripts “0” and “t” mark the values at $\hat{z} = 0$ and $\hat{z} = 1$, respectively. With these variables, equations are now written as

$$\epsilon^2 \frac{d\hat{i}_{io}}{d\hat{z}} = -(\hat{C}/\hat{C}_{ref})^a \sinh \hat{\eta} \quad (4.5)$$

$$\hat{i}_{io} = -\frac{d\hat{\eta}}{d\hat{z}} \quad (4.6)$$

$$\hat{D} \frac{d\hat{C}}{d\hat{z}} = \hat{i} - \hat{i}_{io} \quad (4.7)$$

where

$$\epsilon = \sqrt{\frac{\sigma_{io} b_{ts}}{2 i_*^V l_t^2}} = \frac{l_N}{l_t} \quad (4.8)$$

is the dimensionless Newman's reaction penetration depth or RPD^[67]. This parameter indicates, under ideal transport conditions of gas species, how deep the electrochemical reaction penetrates into the electrode (see **APPENDIX A** and **§§2.3.3**). The dimensionless effective diffusion coefficient of feed gas is given by

$$\hat{D} = \frac{z_e \mathcal{F} D C_t}{\sigma_{io} b_{ts}} \quad (4.9)$$

The system of equations (4.5)-(4.7), which is controlled by three main parameters (ϵ , $\hat{D}$, and $\hat{i}$), describes the spatial distribution of state variables (ionic current, overvoltage, gas concentration, and the rate of electrochemical reaction) in the active layer. From the point of view of SOFC electrochemical performance, the polarization curve of the active layer, expressed through the relation $\hat{\eta}_0 = \hat{\eta}_0(\hat{i})$, is what constitutes our main interest when it is

applied to describe the cell behavior in response to various values of ϵ and $\hat{D}$. The “total” voltage loss (polarization) is given by the value of η_0 at the active layer/electrolyte interface. The shape of the reaction rate, $i_F^\vee(z)$, is also relevant in that it might support the optimization of catalyst design (e.g., load distribution in terms of g cat./cm²) within the electrode

Analytical solutions for the system (4.5)-(4.7) are as yet unknown. Nevertheless, for the limiting cases of ideal ionic transport or ideal gas transport explicit analytical solutions can be derived. In Fig. 3.1 it is shown an example of solution for the case of ideal ionic transport (“gas diffusion-limited case”), whereas in Fig. 3.2 it is shown the case of ideal gas transport (“ionic conduction-limited case”). As discussed in **APPENDIX A**, in both cases an “undisclosed assumption” was made by that Kulikovsky, that the electronic phase of the composite electrode is a perfect conductor. Such assumption can be considered a very good approximation in macroscopic modeling of high-temperature SOFCs (see also §§2.3.2 and §§2.3.3). Also in **APPENDIX A**, it is shown that Kulikovsky’s model for the case gas diffusion-limited case (which is used to evaluate the concentration polarization of a single-cell) is in error, restricting its application to very low current density values.

Figure 4.1: diffusion-limited case: profiles of the ionic current density $\hat{i}_{io}$, feed gas concentration $\hat{C}$, overvoltage $\hat{\eta}$, and the rate of electrochemical conversion $\hat{R}_{OR}$ within the active layer. Parameters used: $\hat{\eta}_0 = 3.0$; $\hat{D} = 0.1$; $\epsilon = 1$; $\hat{t} = 1$; $\hat{C}_{ref} = 1$ (see **APPENDIX A** for details).

Figure 4.2: ionic conduction-limited case: profiles of the ionic current density $\hat{i}_{io}$, overvoltage $\hat{\eta}$, and the rate of electrochemical conversion $\hat{R}_{OR}$ within the active layer. Parameters used were: $\epsilon = 1.0$; (a) $\hat{i} \approx 12.2$; and (b) $\hat{i} \approx 42.4$ (see **APPENDIX A** for details).

One noteworthy result of Kulikovsky's analytical models is that, when solving numerically the full set of equations (4.5)-(4.7), without admitting further simplifications, they predict a condition of negligible concentration polarization associated with an optimal gas diffusion coefficient^[12]. At first, one would expect as sufficient condition for the approximation of ideal gas transport that the gas diffusivity should tend to infinity ($D \rightarrow \infty$). However, at least theoretically, the contribution of gas transport to the cell voltage loss might be neglected if^[12]

$$\hat{D} > \hat{D}_* = \hat{i} \quad (4.10)$$

where $\hat{D}_*$ in dimensional form is given by $D_* = i l_t / (\bar{z}_e \mathcal{F} C_t)$. In other words, there seems to exist an optimal (local optimum) effective gas diffusion coefficient D_* , which provides a near minimal voltage loss in the active layer. At $\hat{D} < \hat{D}_*$ the polarization $\hat{\eta}_0$ decreases rapidly with the growth of $\hat{D}$, whereas for $\hat{D} > \hat{D}_*$ the effect of $\hat{D}$ in lowering the polarization is marginal^[12].

4.3.2 Kulikovsky's Quasi-2D Model of a Single-Cell

Kulikovsky has also developed an analytical model^[255] that takes into account the effect of fuel depletion along the gas channel of a planar SOFC anode (e.g., see Fig. 3.8). In this model, the active layer was modeled applying the analysis described in §4.3.1, but in an integral form, *i.e.* with already-integrated forms of the governing equations (thus without resolving the state variables along the electrode thickness). For this reason, the model may be referred to as a quasi-2D model, because the problem is not solved for simultaneous equations in both spatial directions (gas channel flow direction and cell thickness direction).

This model will be addressed in §4.10.2 as it is more properly regarded as a model for the reactor flow arrangement. As will be seen therein, a critical error exists in Kulikovsky's model. More precisely, there is an erroneous assumption concerning the equipotential condition in the streamwise direction of the cell.

More recently, a similar model to the one developed for a planar SOFC has been applied by Kulikovsky^[251, 256] to study the aging processes occurring non-uniformly along the cathode of a PEM fuel cell. Among the factors that could distort the optimal profile of the local current, thereby affecting the cell polarization curve, Kulikovsky discussed the role of oxygen effective diffusivity variation along the gas channel in lowering the cell limiting current density.

4.4 Single-Scale Models II: Semi-Empirical Analytical Modeling

4.4.1 Parametric Models and Extraction of Physical Parameters

Application of analytical models in parametric modeling and extraction of physicochemical parameters from experiments is ubiquitous in the literature. Not only in SOFC research but probably in all scientific research fields that use mathematical modeling with some sense of practicality. The reason for that is evident: more often than not, relating the various essential quantities by “laws of nature” requires, first, that these quantities are identified by observation, experiment, and *a posteriori* verification. Cases wherein such relations are predicted theoretically prior to its experimental observation are less likely to happen.

In SOFC research there are many examples of this sort, where different measurement techniques and mathematical models have been applied to estimate a multitude of physicochemical parameters. Examples vary from physics-based approaches to purely empirical-based, curve-fitting approaches (e.g., polynomial curve-fitting of experimental data, without regard to the particular form of the equations that describe the physics of the problem). One of the advantages of the physics-based approach is that it is built on the actual mechanisms involved in the electrodic phenomena. That is, by considering a credible description of the actual physical-chemical mechanisms, the fitting process tends to be better resolved, which tends to preclude problems such as the “non-uniqueness” of the fitted solution.

While physics-based models are capable of providing more rigorous description to the problem in question, their numerical solution are often time-consuming, especially for multivariable optimization problems. Thus, obtaining an analytic solution to these models

presents a good compromise, insofar as it can be used to interpret physical processes, while demanding far less computational effort. There are not as many studies in the SOFC literature focusing on concentration losses and that make use of analytical modeling with the above-mentioned goal. Most studies that are built on analytical models aim the extraction of electrokinetic parameters^[257, 258] related to either electrochemical conversion or charge transport in ion/electron conducting materials. Nevertheless, works dealing with the analytical modeling of gas diffusion in SOFCs are still numerous and representative examples will be presented in the following (in §§4.5 studies using non-analytical, physics-based approaches are reviewed).

4.4.2 Effective Porous Diffusion Models (EPDM)

Virkar and coworkers^[82, 259, 260, 261] have developed a number of parametric models based on measurements made on cell materials and components, using traditional electrochemical techniques such as steady-state polarization curves (e.g., E_{cell} vs. i). The essential goal of their models is to evaluate the dependence of polarization effects on various cell parameters, for instance: feed gas composition, including the presence of diluents in the feeding streams; operating temperature; thickness, porosity, and the tortuosity of porous electrodes. It should be note that many of the equations in their theoretical analysis resemble those already examined in §§3.4 and which applied the concept of limiting (or “short-circuit”) current density (i_L). In one of their papers¹, the analysis of concentration polarization starts with the following equations that govern the isothermal transport of gaseous species through porous electrodes, for a mixture of two gases (A and B):

$$\vec{J}_A = -D_A \nabla C_A + y_A \zeta_A \vec{N} - y_A \gamma_A \left(\frac{C_g B_o}{\mu_m^{\text{eff}}} \right) \nabla p \quad (4.11a)$$

$$\vec{J}_B = -D_B \nabla C_B + y_B \zeta_B \vec{N} - y_B \gamma_B \left(\frac{C_g B_o}{\mu_m^{\text{eff}}} \right) \nabla p \quad (4.11b)$$

$$\frac{1}{D_A} = \frac{1}{D_A^{Kn}} + \frac{1}{D_{AB}^{\text{eff}}}, \quad \zeta_A = \frac{D_A^{Kn}}{D_A^{Kn} + D_{AB}^{\text{eff}}}, \quad \gamma_A = \frac{D_{AB}}{D_A^{Kn} + D_{AB}^{\text{eff}}} \quad (4.12a)$$

$$\frac{1}{D_B} = \frac{1}{D_B^{Kn}} + \frac{1}{D_{AB}^{\text{eff}}}, \quad \zeta_B = \frac{D_B^{Kn}}{D_B^{Kn} + D_{AB}^{\text{eff}}}, \quad \gamma_B = \frac{D_{AB}}{D_B^{Kn} + D_{AB}^{\text{eff}}} \quad (4.12b)$$

where $\vec{J}_A$ and $\vec{J}_B$ are diffusive molar fluxes of A and B , respectively; D_{AB}^{eff} is an effective binary diffusivity (e.g., takes into account porosity and tortuosity of porous electrode); D_A^{Kn} and D_B^{Kn} are Knudsen “diffusivities”; C_A and C_B are molar concentrations (mol cm^{-3}); $C_g = C_A + C_B$; y_A

¹ In that work^[82], anode-supported SOFCs were evaluated between 650°C and 800°C with humidified hydrogen as the fuel and air as the oxidant. Button cells were fabricated with YSZ electrolyte ($\cong 10 \mu\text{m}$), LSM/YSZ composite cathode ($\cong 50 \mu\text{m}$), and Ni/YSZ composite anode (having a quite large thickness $\cong 750 \mu\text{m}$).

and y_B are mole fractions; B_o is the porous electrode permeability coefficient; μ_m^{eff} is an effective dynamic viscosity of the gas mixture within the porous medium; p is the total pressure; $\tilde{N}$ is the total molar flux; and the parameters ζ_A , ζ_B , γ_A , γ_B are as defined above.

Equations (4.11a) and (4.11b) are derived from the widely known Dusty-Gas Model or DGM^[63], and the first expressions in Eq. (4.12a) and (4.12b) (for D_A and D_B , respectively) are known as the “Bosanquet formula”^[62]. Despite its long-standing popularity, DGM is a conceptually flawed model^[211, 59, 221] that is based on a number of misleading mathematical derivations. Fortunately, for the models examined herein this will not be a critical issue as many of the conceptual inconsistencies of DGM “disappear” if the pressure gradient term is dropped out from the transport equation, a simplifying procedure that has been, in fact, applied by the authors of the works being reviewed in this section. Although these authors state that the reason for neglecting the pressure gradient is because it is vanishing small, the actual motive is that by dropping this term analytical solutions become possible. However, the pressure gradient cannot be disregarded if chemical reactions take place (see §§3.6 and §§A.5), otherwise mass conservation is violated and the physical consistency of the problem being modeled is lost^[212, 214].

According to DGM, Eq. (4.11a) and (4.11b) are meant to include two flux contributions: a diffusive flux and a “viscous flux”. The diffusive contribution consists of two terms; free molecular or Knudsen “diffusion” (associated with the terms D_A^{Kn} and D_B^{Kn}); and a “continuum part”. For the experimental case under study, Virkar and coworkers assumed that D_A^{Kn} and $D_B^{Kn} \gg D_{AB}^{\text{eff}}$, and thus both D_A and D_B can be replaced by D_{AB}^{eff} . That is, both D_A and D_B approach D_{AB}^{eff} (the effective binary diffusion coefficient) as $\zeta_A | \zeta_B \rightarrow 1$ and $\gamma_A | \gamma_B \rightarrow 0$. Thus, the main contribution to the total flux becomes pure “continuum diffusion”, in the words of that authors. Thus, their analysis is based on the assumption that the dominant contribution to gas transport through the porous electrodes is by mutual diffusion. The effective binary diffusivity (D_{AB}^{eff}) is given by the binary diffusivity (D_{AB}), which is multiplied by the effective porosity (ε) and divided by the tortuosity factor² (τ_*)^[262]. On the cathode side, D_{AB} refers to the binary diffusion coefficient for a mixture of oxygen (O_2) and nitrogen (N_2). On the anode side, D_{AB} is that for a mixture of hydrogen (H_2) and steam (H_2O). The authors assumed that the dependence of binary diffusion coefficient on temperature is not very strong³ ($D_{AB} \propto T^{3/2}$) and this dependence may be accounted for using a model based on the theory of Chapman-Enskog^[263, 264].

² The tortuosity factor τ_* is not to be confused with tortuosity τ [e.g., see [262]]: $\tau_* = \tau^2$.

³ This is not completely correct for polar molecules such as H_2O (e.g., see [264, 33]), especially at high temperatures ($\geq 700^\circ\text{C}$).

In the case of an anode with only H_2 and H_2O (with the partial pressure of O_2 at the anode/electrolyte interface being relatively much lower and thus neglected), and for a fixed total pressure ($\nabla p \cong 0$), Eq. (4.11a) and (4.11b) reduce to

$$\vec{j}_{H_2} = -\frac{D_{an} \varepsilon_{an}}{\tau_{an}^2} \nabla C_{H_2} + y_{H_2} \vec{N} \quad (4.13a)$$

$$\vec{j}_{H_2O} = -\frac{D_{an} \varepsilon_{an}}{\tau_{an}^2} \nabla C_{H_2O} + y_{H_2O} \vec{N} \quad (4.13b)$$

Where $D_{an} = D_{H_2/H_2O}$. Kim *et al.*^[82] made a further simplification in the lines of what was briefly described in §4.3.1: the model disregards the details of what happens within the active layer, which is approximated by an effective zero-thickness model, that is, there is the assumption of a zero-dimensional surface reaction at the electrode/electrolyte interface. This heterogeneous reaction is considered via the following boundary condition, at steady-state (see also Eq. 3.55):

$$|\vec{j}_{H_2}| = |\vec{j}_{H_2O}| = 2 |\vec{j}_{O_2}| = \frac{i}{2eF}, \quad \text{at } z = 0 \quad (4.14)$$

From this equation, one also has that $\vec{j}_{H_2} + \vec{j}_{H_2O} = \vec{N} = 0$. Moreover, if the microstructure of porous electrode is not a function of position and D_{an} is composition-independent, then, after integrating Eq. (4.13a) and (4.13b), the partial pressures of hydrogen ($p_{H_2(ae)}$) and water vapor ($p_{H_2O(ae)}$) at the anode/electrolyte interface are given by

$$p_{H_2}(z=0) = p_{H_2}^{tpb} = p_{H_2(ae)} = p_{H_2}^{bulk} - \frac{\mathcal{R} T \tau_{an}^2 \delta_{an}}{2F D_{an} \varepsilon_{an}} i \quad (4.15a)$$

$$p_{H_2O}(z=0) = p_{H_2O}^{tpb} = p_{H_2O(ae)} = p_{H_2O}^{bulk} + \frac{\mathcal{R} T \tau_{an}^2 \delta_{an}}{2F D_{an} \varepsilon_{an}} i \quad (4.15b)$$

Alternatively, Kim *et al.* assumed that both the porosity and the tortuosity are functions of position, but D_{an} is composition-independent, and then defined an effective anode microstructural multiplier as

$$f_{an} = \frac{\mathcal{R} T}{2F D_{an}} \left(\frac{\tau_{an}^2 \delta_{an}}{\varepsilon_{an}} \right)_{\text{eff}} = \frac{\mathcal{R} T}{2F D_{an}} \int_0^{\delta_{an}} \frac{\tau_{an}^2(z)}{\varepsilon_{an}(z)} dz \quad (4.16)$$

f_{an} is, based on the “First Mean Value Theorem”, the average value of $\tau_{an}^2/\varepsilon_{an}$ on $[0, \delta_{an}]$. The corresponding partial pressures at the electrolyte/electrode interface and the effective binary diffusion coefficient for the anode are now rewritten as:

$$p_{H_2(ae)} = p_{H_2}^{bulk} - f_{an} i \quad (4.17a)$$

$$p_{H_2O(ae)} = p_{H_2O}^{bulk} + f_{an} i \quad (4.17b)$$

$$D_{an}^{eff} = \frac{D_{an} \varepsilon_{an}}{\tau_{an}^2} = \frac{D_{an} \delta_{an}}{(\tau_{an}^2 \delta_{an} / \varepsilon_{an})_{eff}} = \frac{RT \delta_{an}}{2F f_{an}} \quad (4.18)$$

On the cathode side, the flux of nitrogen is zero. Thus, (4.11a) and (4.11b) for a fixed total pressure reduce to

$$\vec{j}_{O_2} = -\frac{D_{ca} \varepsilon_{ca}}{\tau_{ca}^2} \nabla C_{O_2} + y_{O_2} \vec{j}_{O_2} \quad (4.19)$$

For a cathode thickness of δ_{ca} with spatially invariant porosity and tortuosity, the partial pressure of oxygen at the cathode/electrolyte interface is given by, after integrating Eq. (4.19)

$$p_{O_2}(z=0) = p_{O_2}^{tpb} = p_{O_2(ce)} = p - (p - p_{O_2}^{bulk}) \exp\left(\frac{RT \tau_{ca}^2 \delta_{ca}}{4F D_{ca} \varepsilon_{ca} p} i\right) \quad (4.20)$$

For a small cathode thickness, *i.e.* $\delta_{ca} \ll iRT \tau_{ca}^2 / (4F D_{ca} \varepsilon_{ca} p)$, the argument in the exponential is much less than one. Thus, expanding the exponential term and retaining only the first two terms, one obtains a simplified formula:

$$p_{O_2(ce)} \cong p_{O_2}^{bulk} - \left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{RT \tau_{ca}^2 \delta_{ca}}{4F D_{ca} \varepsilon_{ca}} i \quad (4.21)$$

And applying the same rationale as in Eq. (4.16) and (4.17)

$$f_{ca} = \frac{RT}{4F D_{ca}} \left(\frac{\tau_{ca}^2 \delta_{ca}}{\varepsilon_{ca}}\right)_{eff} = \frac{RT}{4F D_{ca}} \int_0^{\delta_{ca}} \frac{\tau_{ca}^2(z)}{\varepsilon_{ca}(z)} dz \quad (4.22)$$

$$p_{O_2(ce)} = p_{O_2}^{bulk} - \left(\frac{p - p_{O_2}^{bulk}}{p}\right) f_{ca} i \quad (4.23)$$

$$D_{ca}^{eff} = \frac{D_{ca} \varepsilon_{ca}}{\tau_{ca}^2} = \frac{D_{ca} \delta_{ca}}{(\tau_{ca}^2 \delta_{ca} / \varepsilon_{ca})_{eff}} = \frac{RT \delta_{ca}}{4F f_{ca}} \quad (4.24)$$

Finally, substituting for the various interface partial pressures in Eq. (2.37) and (2.38), and using Eq. (2.27) yields⁴ the first form of the E_{cell} vs. i curve:

$$E_{cell}(i) = E_{rev}^{bulk} - \eta_{ohm}(i) - \eta_{act}(i) - \eta_{C,an}(i) - \eta_{C,ca}(i) \quad (4.25)$$

$$\eta_{C,an}(i) = -\frac{RT}{2F} \ln\left(1 - \frac{f_{an} i}{p_{H_2}^{bulk}}\right) + \frac{RT}{2F} \ln\left(1 + \frac{f_{an} i}{p_{H_2O}^{bulk}}\right) \quad (4.26)$$

$$\eta_{C,ca}(i) = -\frac{RT}{4F} \ln\left[1 - \left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{f_{ca} i}{p_{O_2}^{bulk}}\right] \quad (4.27)$$

The current density-dependent area-specific resistance (ASR) of the cell may be calculated as the negative gradient of the $E_{cell}(i)$ with respect to i :

⁴Apparently, there is a relevant inconsistency in “Eq. 26” of Kim *et al.*, pp. 73 in [82]. Here their result was modified. See **APPENDIX A** for further details.

$$ASR(i) = -\frac{\partial E_{cell}}{\partial i} = ASR_{ohm} + ASR_{act} + \frac{RT}{4F} \ln \left[\frac{\left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{f_{ca}}{p_{O_2}^{bulk}} + \frac{2 f_{an}/p_{H_2}^{bulk}}{1 - i f_{an}/p_{H_2}^{bulk}} + \frac{2 f_{an}/p_{H_2}^{bulk}}{1 + i f_{an}/p_{H_2}^{bulk}}}{1 - \left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{i f_{ca}}{p_{O_2}^{bulk}}} \right] \quad (4.28)$$

The terms ASR_{ohm} and ASR_{act} are assumed to be current density-independent (the authors also assumed that the activation polarization can be measured as an “effective ohmic resistance”, ASR_{act}). The remaining term, which is current density-dependent, is the contribution of concentration polarization to the cell resistance, $ASR_{conc}(i)$

$$ASR_{conc}(i) = \frac{RT}{4F} \ln \left[\frac{\left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{f_{ca}}{p_{O_2}^{bulk}} + \frac{2 f_{an}/p_{H_2}^{bulk}}{1 - i f_{an}/p_{H_2}^{bulk}} + \frac{2 f_{an}/p_{H_2}^{bulk}}{1 + i f_{an}/p_{H_2}^{bulk}}}{1 - \left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{i f_{ca}}{p_{O_2}^{bulk}}} \right] \quad (4.29)$$

When $i = 0$, the $ASR_{conc}(i)$ reduces to

$$ASR_{conc}(0) = \frac{RT}{4F} \ln \left[\left(\frac{p - p_{O_2}^{bulk}}{p}\right) \frac{f_{ca}}{p_{O_2}^{bulk}} + \frac{2 f_{an}}{p_{H_2}^{bulk}} + \frac{2 f_{an}}{p_{H_2O}^{bulk}} \right] \quad (4.30)$$

which is nonzero, indicating that the effect of concentration polarization persists even at the open-circuit limit. As is evident from Eq. (4.30), the lower the $p_{H_2O}^{bulk}$, i.e., the drier the incoming fuel, the greater is the $ASR_{conc}(0)$, and the greater is the initial concavity in the E_{cell} vs. i curve.

The final step in the paper of Kim *et al.*^[82], the authors apply the same rationale as already described in §3.4.1 for the obtainment of the limiting current density (i_L). In the case of an anode-supported cell, the authors have derived the following results:

$$i_{L,an} = i_{as} = \frac{2F p_{H_2}^{bulk} D_{an}^{eff}}{RT \delta_{an}} \quad (4.31)$$

$$i_{L,ca} = i_{cs} = \frac{4F p_{O_2}^{bulk} D_{ca}^{eff}}{RT \delta_{ca}} \left(\frac{p - p_{O_2}^{bulk}}{p} \right)^{-1} \quad (4.32)$$

And in terms of i_{as} and i_{cs} , the concentration polarization resistance at OCV is now given by

$$ASR_{conc}(0) = \frac{RT}{4F} \ln \left[\frac{1}{i_{cs}} + \frac{2}{i_{as}} \left(1 - \frac{p_{H_2}^{bulk}}{p_{H_2O}^{bulk}} \right) \right] \quad (4.33)$$

Here, again, it is noted that the drier the incoming fuel, the large is $ASR_{conc}(0)$. Rewriting Eq. (4.25) with the results above yields:

$$E_{cell}(i) = E_{rev}^{bulk} - i ASR_{ohm} - a - b \ln i + \frac{RT}{4F} \ln \left(1 - \frac{i}{i_{cs}} \right) + \frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left(1 + \frac{i p_{H_2}^{bulk}}{i_{as} p_{H_2O}^{bulk}} \right) \quad (4.34)$$

wherein a Tafel kinetics was selected to describe the relation between i and η_{act} ,

$$\eta_{act}(i) = a_{tc} + b_{ts} \ln i, \quad a_{tc} \approx -\frac{RT}{4\alpha F} \ln i_0, \quad b_{ts} \approx -\frac{RT}{4\alpha F} \quad (4.35)$$

However, in the work of Kim *et al.*^[82], a_{tc} and b_{ts} were treated simply as empirical constants, fitted from experimental data using various E_{cell} vs. i curves (see Table 4.1). The authors also used the above equations in order to study the shape of the E_{cell} vs. i curves (e.g., by evaluating the sign of the second order derivative, $\partial^2 E_{cell}/\partial i^2$). They have identified characteristic regions of nonlinear concave-up curvature ($\partial^2 E_{cell}/\partial i^2 \geq 0$) at low current densities, and convex-up curvature ($\partial^2 E_{cell}/\partial i^2 \leq 0$) at higher current densities. They noted, however, that the eventual transition from an initial concave-up curvature (at low current densities) to a convex-up curvature (at higher current densities), depends on the relative importance of the activation polarization and concentration polarization. They finally concluded that, in anode-supported cells, a significant contribution may well arise from concentration polarization resulting from the resistance to gas transport through thick porous electrodes.

Table 4.1: Measured and fitted parameters for anode-supported cell (Kim *et al.*^[82]).

Measured				
Temperature (°C)	650	700	750	800
$ASR(0)$ ($\Omega \text{ cm}^2$)	0.569	0.428	0.332	0.261
Fitted using Eq. (4.34)				
a_{tc} (V)	0.0923	0.0628	0.054	0.050
b_{ts} (V)	0.031	0.0281	0.0248	0.0247
i_{as} (A cm^{-2})	3.18	4.74	4.95	5.65
Calculated				
$RT/4F$ (V)	0.01988	0.02096	0.02204	0.0232
i_0 (A cm^{-2}), Eq. (4.35)	0.051	0.107	0.113	0.132
$ASR_{conc}(0)$ ($\Omega \text{ cm}^2$), Eq. (4.33)	0.417	0.31	0.297	0.273
D_{an}^{eff} (cm s^{-1}), Eq. (4.18)	0.096	0.151	0.166	0.199

In their latter papers Virkar and coworkers apply, essentially, the same mathematical formalism as described in the preceding pages (that is, on what strictly concerns the topic of concentration polarization). In studying the fuel composition and diluent effect on gas transport of anode-supported SOFCs^[259], they modified Eq. (4.13) to include an additional gas component (the diluent, either of He , N_2 , H_2O , or CO_2) in order to model a ternary gas mixture

on the anode side. For instance, in the case of the anodic limiting current density they obtained:

$$i_{as} = \frac{2\mathcal{F} p_{H_2}^{bulk,in} D_{an}^{eff}}{RT \delta_{an}} \left(1 + \frac{D_{an}^{eff}}{RT \delta_{an}} \frac{A_{an} p}{\tilde{m}_T} \right)^{-1} \quad \text{or} \quad D_{an}^{eff} = i_{as} \left(\frac{2\mathcal{F} p_{H_2}^{bulk,in}}{RT \delta_{an}} - \frac{i_{as}}{RT \delta_{an}} \frac{A_{an} p}{\tilde{m}_T} \right)^{-1} \quad (4.36)$$

where A_{an} is the electrode geometric area (cm^2); $\tilde{m}_T$ is the total molar flow rate of fuel and diluent (mol s^{-1}); and $p_{H_2}^{bulk,in}$ is the initial (incoming fuel) partial pressure of H_2 . In another paper^[260] they studied SOFCs that were fabricated with interlayers in-between the anode and electrolyte, and cathode and electrolyte (thus making two additional layers in comparison to their previous work). They evaluated the effect of various parameters on cell performance, namely: electrolyte thickness, interlayer thickness, support thickness, and support porosity. In this work, however, the authors did not apply the concept of limiting current. Instead, they have calculated the concentration polarization by using gas partial pressures directly in Eq. (2.37)-(2.38). The partial pressures at the electrode/electrolyte interface were calculated using a modified model that accounts for the additional layer. For instance, the hydrogen partial pressure was given by:

$$p_{H_2}(z = 0, i) = p_{H_2(ae)}(i) = \frac{\delta_{an(2)}}{D_{an(2)}^{eff}} \left[\frac{p_{H_2}^{bulk} D_{an(2)}^{eff}}{\delta_{an(2)}} - \frac{i \mathcal{R} T \delta_{an(1)}}{2\mathcal{F} D_{an(1)}^{eff}} \left(\frac{D_{an(2)}^{eff}}{\delta_{an(2)}} + \frac{D_{an(1)}^{eff}}{\delta_{an(1)}} \right) \right] \quad (4.37)$$

$\delta_{an(1)}$ and $\delta_{an(2)}$ are, respectively, the anode support and the anode functional layer thicknesses; $D_{an(1)}^{eff}$ and $D_{an(2)}^{eff}$ are, respectively, effective binary diffusivities through the anode support and anode functional layer, which were fitted from experimental data. In their latter work^[261], however, effective binary diffusivities $D_{an(1)}^{eff}$ and $D_{an(2)}^{eff}$ were measured in a special electrochemical concentration cell^[265].

A number of other authors have been adopting a similar macroscopic approach to the presented above. Gopalan and coworkers^[266] used the same concentration polarization model to evaluate the polarization on single-step co-fired SOFCs and to support the analysis^[267] of “out-of-cell” measurements of H_2 - H_2O effective binary diffusivity in the porous anodes, at different temperatures. Chan *et al.*^[268] has applied a very similar model in order to study the polarization sensitivity to the change of cell component thickness. Among the minor differences, the latter author did not simplify Eq. (4.20), *i.e.*, the exponential term was kept as it is. Using a canonical Fick diffusion equation, Huang^[134] has derived theoretical expressions accounting for the gas diffusion in a tubular cathode (*i.e.*, using a cylindrical coordinate system), including an equation for the limiting current density, based on the same assumption from Virkar and other authors that, at this current level, the interfacial partial pressure of the

reacting gas reaches zero. Aguiar *et al.*^[269] used Eq. (4.15a), (4.15b), and (4.20) in the simulation of a CH_4 -fueled planar SOFC (stack) with direct internal reforming. Here, the authors considered all reforming reactions to occur before the SOFC electrode.

There are works in the literature that have also considered, at least in part, the analytical models originally derived by Virkar and coauthors, but they introduced a number of noteworthy modifications. Among these works, there exist those^[270, 271, 272, 273] that have set out, more properly, reviews about the available models on gas diffusion and diffusivity measurement in porous electrodes of SOFCs. All of them perform some level of critical analysis by comparing alternative mass transfer models, for instance: traditional Fick model; modified Fick model (MFM); canonical Maxwell-Stefan (MSM) model; modified MSM; and DGM, among others. Finally, there are works that have discussed specific features (*e.g.*, limitations) of the effective porous diffusion model (EPDM) developed by Virkar and coauthors, proposing modifications and/or extensions. Some of these works are briefly considered in the following paragraphs.

Schmidt and Tsai^[135] criticize commonly made approximations in diffusion equations, such as uniform total gas pressure within the anode and the assumption of zero feed gas concentration at the anode–electrolyte interface, under current saturation condition. The authors propose a method to eliminate the latter approximation, and by doing so they claim that physically reasonable values of tortuosity are now obtained, even at low current limit. With their semi-analytical model (a transcendental algebraic equation), tortuosity values can be found from saturation currents, or vice-versa.

In order to study the effect of pressure gradient on mass transfer in an SOFC anode, Grigoruk and Kasilova^[274] have developed a simplified, one-dimensional mass transport model based on DGM, for which an analytic solution is obtained in the case wherein the fuel is not diluted by an inert component (they consider a two-component gas mixture). In essence, this model is akin to that of Virkar and coworkers, with the exception that in Eq. (4.11a) and (4.11b) the simplifying conditions $\zeta_A | \zeta_B \rightarrow 1$ and $\gamma_A | \gamma_B \rightarrow 0$ are not aprioristic assumed. However, Grigoruk and Kasilova have also neglected the pressure gradient in the derivation of their mathematical model and thus the claims of these authors are constructed based on comparisons with the numerical solution of the “complete” DGM equations. Part of their model development is, therefore, based on misleading assumptions steaming from the errors of DGM.

Brus *et al.*^[275] estimated the tortuosity for SOFC anodes using an EPDM-based model and saturation (limiting) current densities as a fitting parameter. They compared the results from this mass transfer model with tortuosity values obtained through an alternative method,

which applied the structural analysis of a “real” three-dimensional sample micro-structure, reconstructed using a combination of scanning electron microscope and focus ion beam milling (FIB-SEM). Their work indicates that the EPDM has significant limitations in estimating tortuosity values for anodes running far from the current saturation condition. According to the authors, in this condition the model requires relatively thick anode and very low concentration of hydrogen (e.g., high fuel utilization), and hence can only be used for raw estimation of tortuosity values. They claim that the main reason for the overestimation of tortuosity is the assumption of zero hydrogen partial pressure at the electrode/electrolyte interface.

Bao *et al.*^[276] have developed a macroscopic model for synthesis gas (syngas) fueled SOFC anodes, including an analytical model for H_2/CO electrochemical co-oxidation. They used an analytical approximation^[277] to describe charge and mass transfer as decoupled processes, which can provide analytical profiles of both voltage losses and gas species concentration along the anode thickness. In these analytical approximations, the molar fraction of feed gas is shown to be explicitly dependent on electrochemical variables. Their paper also provided verification of modeling results with experimental measurements (see Fig. 4.3), based on which the model has shown good correlation at high fuel utilization, when keeping a fixed porosity/tortuosity ratio. Differently from Virkar and coworkers^[82] who have estimated the limiting current density at the low inlet fuel concentration (20% H_2), Bao *et al.*^[276] have instead estimated the limiting current density at high inlet fuel concentration (97% and 85% H_2).

Figure 4.3: comparison between experimental E_{cell} vs i curves and computations. $H_2 - H_2O$ binary system simulated using analytical MSM (Maxwell-Stefan Model) with different porosity/tortuosity factor ratios, and two simplified models for the fuel gas channel, namely “logmean” and “inlet” (figure reproduced from [276]).

Drescher *et al.*^[278] implemented a distinct approach in comparison to the ones presented above. In this work, the goal of these authors was not to study the electrochemical performance of the SOFC, but to characterize the influence of mass transfer limitations in the methane reforming reactivity within a *Ni-YSZ* anode as a function of the anode thickness. Much like as in a “thought experiment” where only the anode is included in the experimental “cell” (e.g., see similar work in [279]). The authors investigated structural properties of SOFC anodes through gas adsorption, diffusion, and permeation measurements, using a modified Wicke–Kallenbach diffusion cell^[280]. More precisely, they applied the mean transport pore model (MTPM)^[281] to correlate the measured permeation (B''_{MPTM}) with the mean transport pore radius ($\langle r_p \rangle$) and the ratio of porosity (ε) to tortuosity (τ), according to Eq. (4.38). In a latter paper^[282] these authors studied a complete single-cell, applying the same MTPM model and once again focusing on the gas transport and methane reforming reactions in SOFC anodes.

$$B''_{MPTM} = \frac{\varepsilon}{\tau^2} \left(\frac{\pi}{4} \langle r_p \rangle \bar{u}_T + \frac{\langle r_p^2 \rangle}{8\mu_m} p \right) \quad (4.38)$$

where $\bar{u}_T$ is the mean thermal velocity of the gas^[281].

More recently, an EPDM-based model was developed to account for the gas leak diffusion-induced polarization^[283], especially for μ -SOFCs that suffer from problems related to non-tight electrolytes. These authors have investigated, on theoretical grounds, the gas leak through “microstructural flaws” (cracks and pinholes) of thin electrolytes and its effects on concentration polarization for both anodes and cathodes. They derived algebraic expressions for the evaluation of limiting current densities and concentration polarizations, which are similar in spirit and purpose to Eq. (4.31), (4.32), and (4.34).

In short, the models reviewed in this section employ some degree of parametric modeling through analytical solutions of governing and constitutive equations. They aim the obtainment of accurate expressions that relate the gas-phase composition at the fuel and air channels with the composition at the three-phase-boundary, where all important electrochemical phenomena take place. The virtue of these models are that they apply a macroscopic approach befitting the spatial and time resolution of the available experimental information, thus without introducing unnecessary (often obscure) level of sophistication into the mathematical models.

4.5 Single-Scale Models III: Multiphysics Macro-Homogeneous Approach

In §§1.4.2 it was described what are the main features of a multiscale approach^[1, 2] and to what extent this approach is necessary in order to accurately represent the performance of all components of a SOFC. More specifically, multiscale modeling is often needed in those problems where single-scale models are incapable of making spatio-temporal resolved assessments of the complex interplay of competing, physicochemical microscopic processes. That is, when the interaction of physicochemical processes on “fine-scales” leads to significant spatial and time heterogeneities in the state variables of interest, ultimately affecting phenomena at “coarse-scales”. Furthermore, these heterogeneities happen to be very difficult (or even impossible) to model “on average” on this “coarse-scale”. Thus, the proper resolution of two or more dissimilar scales at which those processes take place becomes pivotal in selecting a modeling technique(s). In this sense, models to be described in this section are considered applicable to problems in which, supposedly, the “macro-averaging” of the details of an underlying microscopic world is still valid or accurate enough. Before proceeding to the review of the so-called macro-homogenous models, it is important to dedicate few words to what is meant when one conveniently labels a model as “single-scale” or “multiscale”^[40]. Some words of Fish^[155] are given in this direction:

(...) Equations can be classified into two categories: those that directly follow from physical laws and those that do not. A constitutive equation demonstrates a relation between two physical quantities that is specific to a material or substance and does not follow directly from physical laws. It can be combined with other equations to solve specific physical problems. (...) Phenomenological modeling relates several different empirical observations of phenomena to each other in a way that is consistent with fundamental theory but is not directly derived from it. (...) An alternative to phenomenological modeling is to derive constitutive equations (or directly, field quantities) from finer scale(s) where established laws of physics are believed to be better understood. The enormous gains that can be accrued by **this so-called multiscale approach** have been reported in numerous articles. ([155], pp. 1-2) — this author's emphasis in bold letters.

Therefore, one could say that even if all governing equations (“physical laws”) describe processes on a single-scale, if constitutive equations (or “constitutive laws”⁵) and constitutive parameters are obtained from other scales (not necessarily from finer scales, even though this is often the case), one may refer to this combination as a multiscale approach. Under the

⁵Term originally coined by Walter Noll [419]. One could label all that one does not fundamentally know about a boundary value problem as a “constitutive law”, though this may result in ambiguity.

definition above, however, there is a fair dose of subjectivity in classifying a model as “single-scale” or “multiscale”. Firstly, because it is not the governing equations what that necessary need to be solved on multiple scales so that the approach can be called multiscale; secondly, phenomenological constitutive equations are not necessarily macroscopic-based derivations; on certain cases, one can derive phenomenological equations on finer scales as well and apply them (“upscaled”) on coarser scales. In other words, it is not the fact that a constitutive equation is eventually based upon empirical (or numerical) observations of phenomena that makes it “non-multiscale”. One concrete example is that of phenomenological chemical kinetics (mean-field approximation) that employs Arrhenius-like exponential formulas: parameters in these formulas can be derived, for instance, from either macroscopic or microscopic experiments, or even from “microscopic theories” such as UBI-QEP or DFT^[93]. In the latter case, does it make the modeling technique a multiscale approach? Certainly, there is a nuance in answering this question that depends on personal views/biases.

In this dissertation, specifically, gas-phase phenomena are the focus. Thus, the terms “single-scale” or “multiscale” will refer only to these phenomena, even if a work from the literature may have applied multiscale techniques to other coexistent physicochemical processes (*e.g.*, electrochemistry) in the same analysis. Thus, for gas-phase phenomena, either governing equations or constitutive relations must have been derived considering information from more than one physical scale in order to be classified as multiscale. Another example: if transport parameters such as porosity and tortuosity (or equivalently, the effective diffusivity) are obtained via mesoscale models, *e.g.* Lattice-Boltzmann Method (LBM), on a real porous microstructure, but afterwards macroscopic continuum equations such as Eq. (4.13a) are used, herein this technique will be referred to as multiscale. On the other hand, if the same parameters are obtained from the literature or by “best-fitting” their values from macroscopic experiment data, here this technique will be referred to as single-scale. Furthermore, just because macroscale-continuum equations may eventually describe simultaneous processes that have different length and time scales (quite common in chemically reacting systems with short-lived, intermediate chemical species), this does not make the technique multiscale (just the problem being tackled). The assertion remains true if more equations are added to take into account adsorption phenomenon, but they are all solved on the same macroscopic scale. As alluded to above, however, this classification is subjective and reflects the way in which the author decided to organize this monograph.

In the SOFC literature, most of the publications on the subject of numerical simulations are those that use single-scale, macro-homogeneous models of porous layers. The number is indeed overwhelming when compared to other modeling approaches. Without ascertaining the

reasons for that, it is probable that macro-homogeneous models have been the best available “benefit-cost” solution until recent days. It was said “until recent days” because existing research paradigms are now changing vigorously due to the flourishing of applied nanosciences. For instance: access to high performance computing; greater dissemination (and consolidation) of novel multiscale modeling techniques; further development of computational material sciences in response to the need to “design on the nanoscale”; and so forth, are factors driving several researchers towards alternative modeling approaches. As for many things, there is no “one-size-fits-all” solution and as necessities and/or requirements change, solutions will get more diverse, more complex. Thus, at least two trends are likely to unfold: (i) the macro-homogeneous approach will share space with other distinct approaches; and (ii) the macro-homogeneous approach itself will get more complex; it will ameliorate due to the demands of a better description of the microscopic world. Certainly, this approach will not disappear.

Having said that the number of publications is enormous, it would be impossible to perform an encompassing review of all works that have been using a macro-homogeneous approach to model SOFCs. Thus, this work describes a selection of mathematical models that may well represent the class of macro-homogeneous models for SOFCs; more precisely those concerning gas-phase phenomena and the effects related to concentrations polarization. There is, however, a complicating factor that can make the discussion of some models difficult. Several independent research groups re-develop pre-existing models from the literature, by including modifications to the previous model. As the implementation of the previous model (*i.e.*, its computational source code) is not available to new researchers, these mathematical models are very seldom compared to each other, thereby making it impossible to assess the significance of the proposed modifications. Furthermore, most mathematical models in the SOFC literature do not follow thorough validation processes (*e.g.*, get verified by third-parties).

4.5.1 Macro-Homogeneity of Field Equations in an Inhomogeneous Continuum

The expression “macro-homogeneity of field equations in an inhomogeneous continuum” conveys at least two important assumptions. The first is that the equations being solved disregard the microscopic details of SOFC porous layers. More precisely, constitutive equations perform an incomplete description of the real complex, inhomogeneous pore structure, whose properties (geometric and others) are now described in a zero-dimensional space (*i.e.*, homogeneous). Of course, one hopes that this approach still allows capturing the macroscale behavior, that is, according to certain transformations it will preserve macroscopic

properties. The second meaning is that the (undoubtedly discrete) porous medium is now considered as a “new continuum”, interpenetrated with the continuum of the gas-phase. Thus, not only thermodynamic and transport properties of the porous material are lumped because of the homogenous assumption, but they are “homogenized” together with those of gas species.

To be sure, this makes one wonders about what are the practical consequences of this “loss of information”, besides losing spatial resolution and ignoring the fluctuating part of the fields of state variables. These issues will not be addressed herein; nevertheless, at this point some considerations are highlighted so to emphasize the limits and critical features of macro-homogeneous models^[67, 155, 284, 205].

- Although on the microscopic scale there is a “well-defined” interface (whose geometry is very complex) between the gas and pore-wall, in order to obtain results of practical significance the macro-homogeneous model only describes the macroscopic features of a porous electrode. That is, the model should represent some suitable average over the random and complicated microscopic geometry of the porous electrode and this representation should be reasonably accurate on the macroscale.
- Superficial current densities and species fluxes must be corrected for the specific interfacial areas (a_s) involved, or for the TPB specific length (λ_{tpb}), in order to correctly evaluate the current density or flux at a particular phase boundary.
- One should expect macro-homogeneous models to fail when a length characteristic of the microstructure (e.g., pore radii) becomes comparable to a length characteristic of the macrostructure size of the electrode (e.g., its thickness or, alternatively, the reaction penetration depth).
- Macro-homogeneous models often consider that there is no actual variation of gas concentration across the pore diameter. This variation is usually neither explicitly described nor accounted for at all.
- The characteristic time for gas-phase diffusion, e.g. $(\delta_{an}/\hat{l}_v)^2/D_{an}^{eff}$, is usually assumed to be far more than the characteristic time for charging the double-layer capacity, e.g. the ratio $D_{an}^{eff} a_s C_{dl}/\sigma_{io} \ll 1$. This ratio is expected to be greater than one for very high interfacial areas and low ionic conductivities. In HT-SOFC electrodes, the double-layer relaxation time is in the range^[8] of 10^{-5} to 10^{-4} s .

Based on the following review one should apprehend how, within the limits of a macro-homogeneous approach, each model delineates its constitutive equations and parameters. This aspect is what will, for the most part, differentiate one model from another. An additional differentiation criterion is whether a multiphysics approach is used or not, e.g., if gas-phase macro-homogeneous equations are coupled to chemical kinetics and/or to charge transport.

4.5.2 Macro-Homogeneous Models of Porous SOFC Layers

4.5.2.1 Ferguson *et al.*

Ferguson *et al.*^[285] developed one of the earliest three-dimensional numerical simulations of SOFCs, using macro-homogeneous partial-differential equations. Their numerical code was able to perform the computation of the local distributions of the electric potential, temperature, and concentration of the chemical species, in order to show the behavior of these distributions when certain parameters (e.g., geometry of the cell, electrolyte materials, and temperature in the channels) are varied. The authors studied natural gas-fed and hydrogen-fed SOFCs under stationary regime, for different unit cell designs, such as planar, tubular, and cylindrical geometries. For the planar concept, specifically, they have also considered three alternative configurations, namely co-flow, counter-flow, and cross-flow gas channel arrangements. The aim of their work was, besides the development of the numerical code and its validation with experimental data, to compare the cell efficiency for the cases of parallel (co-flow) and cross-flow designs; and then to assess the influence of the electrode thickness on cell efficiency. Differently from previously published works, Ferguson and coauthors^[285] have modeled the spatial variation of the cell variables within the unit cell (PEN sandwich) itself, whereas in other prior works the stack was modeled assuming the solid materials to be all at the same temperature and the current density being computed by averaging the conductivities of the various cell components. Ferguson and coauthors were pioneers in building a two-dimensional model for the cell cross-section (which amounts to a three-dimensional model globally). Modeling equations, boundary conditions, and a number of remarks/assumptions are presented in Table 4.2.

Table 4.2 Macro-homogeneous model from Ferguson *et al.* [285]

Table 4.2 Macro-homogeneous model from Ferguson <i>et al.</i> [285]		
Governing Equations (“Conservation Laws”)		
$\nabla \cdot \mathbf{i} = \dot{S}_{V,i}$	in interconnector, anode, electrolyte, and cathode	(4.39a)
$\nabla \cdot \tilde{\mathbf{N}}_k = \dot{S}_{V,y_k}$ for $k = O_2, N_2$ in air channel and cathode for $k = H_2, H_2O, CO, CO_2, CH_4$ in fuel channel and anode	in fuel channel, anode, cathode, and air channel	(4.39b)
Constitutive Equations and Parameters		
$\vec{i} = -\sigma \nabla \phi$	in interconnector, anode, electrolyte, and cathode	(4.39c)
$\tilde{\mathbf{N}}_k = -C_g D_{k,mix} \nabla y_k + y_k \sum_{j \in \mathcal{N}_{gas}} \tilde{\mathbf{N}}_j$ for $\mathcal{N}_{gas} = \{O_2, N_2\}$ in cathode for $\mathcal{N}_{gas} = \{H_2, H_2O, CO, CO_2, CH_4\}$ in anode	in anode and cathode	(4.39d)

CONTINUATION OF TABLE 4.2		
$\vec{N}_k = -C_g \vec{u}_{l,mix} y_k$	in l , for $l = \{\text{fuel channel, air channel}\}$	(4.39e)
$\sigma \text{ (}\Omega^{-1} \text{ m}^{-1}\text{)} = \begin{cases} 4 \times 10^7 / T \exp(-1200/T) & , \text{ in cathode} \\ 3.34 \times 10^4 / T \exp(-10300/T) & , \text{ in anode} \\ 9.5 \times 10^7 / T \exp(-1150/T) & , \text{ in electrolyte} \\ 9.3 \times 10^5 / T \exp(-1100/T) & , \text{ in interconnect} \end{cases}$		(4.39f)
Source Terms		
$\dot{S}_{v,i} = 0$	in interconnector, anode, electrolyte, and cathode	(4.39g)
$\dot{S}_{v,y_k} = \begin{cases} 0 & , \text{ in cathode and air channel} \\ v_{k,sh} \dot{S}_{sh} + v_{k,re} \dot{S}_{re} & , \text{ in anode and fuel channel} \end{cases}$		(4.39h)
Interface Conditions ("Internal Boundary Conditions")		
$[\vec{N}_{O_2} \cdot \vec{n}]_{ca} = \frac{[\vec{i} \cdot \vec{n}]_{elyt}}{4\mathcal{F}}$	, at cathode/electrolyte interface	(4.39i)
$[\vec{N}_{H_2} \cdot \vec{n}]_{an} = \frac{[\vec{i} \cdot \vec{n}]_{elyt}}{2\mathcal{F}}$	, at anode/electrolyte interface	(4.39j)
$\phi_{ca} - \phi_{elyt} = \frac{RT}{4\mathcal{F}} \ln(y_{O_2}) - ASR_{act,ca} [\vec{i} \cdot \vec{n}]_{elyt}$	, at cathode/electrolyte interface	(4.39k)
$\phi_{elyt} - \phi_{an} = -\frac{\Delta_r G^\circ}{2\mathcal{F}} - \frac{RT}{2\mathcal{F}} \ln\left(\frac{y_{H_2O}}{y_{H_2}}\right) - ASR_{act,an} [\vec{i} \cdot \vec{n}]_{an}$	, at anode/electrolyte interface	(4.39l)
External or Domain Boundary Conditions		
$\nabla \phi \cdot \vec{n} = 0$	, at the interface between air channel (or fuel channel) and solid walls	(4.39m)
$[\vec{i} \cdot \vec{n}]_{an} = i_{avr}$	, at anode/current collector interface (or cathode/current collector interface)	(4.39n)
Finally, the boundary conditions on y_k and ϕ are imposed at the inlet face of the gas channels (external boundary of the cell), and they depend on the chosen operating conditions.		
Assumptions and Remarks		
<ul style="list-style-type: none"> i. The fluxes $\vec{N}_k$ and $\vec{i}$, and the source terms $\dot{S}_{v,y_k}$ must be related to the unknowns y_k and ϕ. ii. The electrochemical reactions are assumed to occur at the anode/electrolyte and cathode/electrolyte interfaces (<i>i.e.</i> heterogeneous reactions are modeled through boundary conditions). iii. The conservation of electrons was written at the interfaces where the electrochemical reactions occur and the mass flux is related to the electric current by Faraday's law. iv. The electric potential is continuous throughout the solid parts, except at the electrode/electrolyte interfaces, where electrochemical reactions occur. Potential jumps were modeled using Nernst equation. v. It was assumed that no chemical reactions occur within the air channel. vi. Reforming and water-shift reactions were assumed to occur within the fuel channel and anode domains. vii. In the porous media (<i>i.e.</i>, cathode and anode), the molar fluxes were assumed to satisfy a type of "Fick's law" of diffusion for a gas mixture ("multicomponent mixture extension of Fick's law"). 		

CONTINUATION OF TABLE 4.2

- viii. It was assumed that in the gas channels the molar flux is mainly convective in the flow direction (Eq. [4.39e]). Diffusive mass exchange at the boundaries with electrodes were taken into account using a mass-transfer coefficient. However, no additional information was provided by Ferguson *et al.*^[285] on how this was actually accomplished.
- ix. The volumetric source term $\dot{S}_{v,y_k}$ is made up of two terms, $\dot{S}_{sh}$ and $\dot{S}_{re}$, which are the rates of reaction of water gas-shift (WGS) and methane reforming reactions, respectively; $\nu_{k,sh}$ and $\nu_{k,re}$ are the net stoichiometric coefficients of the species k in question in WGS and reforming reactions, respectively (positive for products, negative for reactants).

One can verify that in the species mass transport equations the nature of the porous medium is completely absent. The single possible “vestige” that could indicate that a porous medium is being modeled is the constitutive parameter $D_{k,mix}$ in Eq. (4.39d). Nonetheless, Ferguson and coauthors do not provide any information concerning this parameter, beyond saying that it is “the diffusion coefficient of the k -th species in the considered mixture” (see pp. 112 in [285]). Most likely, this parameter was fitted from experimental data, although $D_{k,mix}$ values were not made available in their paper. Furthermore, the physical definition of the total molar flux $\vec{N}_k$ in Eq. (4.39d) is unknown, *e.g.*, is it a cross-section averaged, superficial flux calculated based on the fraction of open area of porous medium? Or is it the flux associated with the “bulk” flow within the pore space?

The model by Ferguson *et al.* serves the purpose of introducing one important aspect that this dissertation tries to address: that in the SOFC literature, quite frequently, no matter how simple or how complex, either consistent or erroneous a model may be, experimental data are always, seemingly, verified. For example, if a model has an awkwardly large number of adjustable parameters, the likelihood that this model will match empirical observations is potentially high, even though it is revealed afterwards that these fitted parameters are disproved of physical meaning (*i.e.*, they are “fudge factors”). When attributing “unphysical” values to those adjustable parameters only shows that the model is able to represent experimental data, much like a 4th order polynomial fitting-formula would. Although the presence of a “large number of adjustable parameters” is an expected characteristic of macro-homogeneous models, when a number of works in the literature allegedly capture “quasi-microscopic” features of SOFCs electrodes using these “crude models”, then the underlying reason for this successful accomplishment is not clear^[58].

4.5.2.2 Yakabe *et al.*

Yakabe *et al.*^[286] developed a mathematical model to simulate an anode-supported planar (counter-flow design) SOFC. Concerning the concentration polarization, they have simulated the three-dimensional distribution of the gaseous species for binary systems (H_2-H_2O and $CO-CO_2$) and also for multicomponent mixtures. In this latter case, the model has considered the use of steam-reformed methane as fuel, for which the concentration polarization, at high fuel utilization, was estimated. In order to model flow phenomena, the authors assumed the validity of Darcy's Law in the porous medium (to account for the "viscous flow" parcel and also to define a constitutive equation for the pressure gradient term) and that reactant species are transported to the electrolyte/anode interface mainly by mass diffusion. As it seems, their analysis of multicomponent diffusive transport^[287, 288] is based on certain results derived from parallel pore models^[289, 290, 213], which by their turn rely on a number of assumptions made in the earlier versions of DGM developed by Evans and Manson^[291] for binary gas systems. Table 4.3 includes information on the mathematical model used by Yakabe and coauthors. However, it should be noted already that they have provided scarce description about their actual CFD model (e.g., there are no explicit references to governing and constitutive equations, source terms, and boundary conditions).

Table 4.3: Macro-homogeneous model from Yakabe <i>et al.</i> [286].			
Governing Equations Coupled to Constitutive Equations (<i>i.e.</i> , Transport Equations)			
$\nabla p = -\vec{\mathfrak{B}} \vec{u}_s$	in anode	(4.40a)	
Constitutive Equations and Parameters			
$D_k^{\text{eff}} = \frac{\varepsilon}{\tau^2} \left(\frac{1 - \varpi_{km} y_k}{D_{km}} + \frac{1}{D_k^{Kn}} \right)^{-1}$ (for $k = H_2, H_2O, CO, CO_2, Ar$)	where ⁶ $\varpi_{km} = 1 - M_{\Delta n, k} = 1 - \left(\frac{M_k}{\bar{M}_n} \right)^{1/2}$	in anode	(4.40b)
$D_k^{Kn} = \langle r_p \rangle \frac{2}{3} \left(\frac{8 \mathcal{R} T}{\pi M_k} \right)^{1/2}$		in anode	(4.40c)
$D_{km} = \frac{1 - y_k}{\sum_{j \neq k} \left(\frac{y_j}{D_{k,j}} \right)}$ (for $j = H_2, H_2O, CO, CO_2, Ar$)		in anode	(4.40d)
The binary gas diffusion coefficient $D_{k,j}$ was calculated using a standard Chapman–Enskog theory ^[263] .	in anode	-	

⁶ The number-average molar mass ($\bar{M}_n$) is given by: $\bar{M}_n = \sum_k y_k M_k$ (whereas the mass-average molar mass is given by $\bar{M}_w = \sum_k x_k M_k = \sum_k y_k M_k^2 / \bar{M}_n$).

CONTINUATION OF TABLE 4.3					
Porosity ε (%):	46	Isotropic permeability $\mathfrak{B}$ (Pa s m ⁻²):	1.7x10 ⁻¹⁰	in anode	-
Tortuosity factor τ^2 :	4.5	Average pore size $\langle r_p \rangle$ (μm):	2.6		
Thermodynamic Formulae					
$\eta_{conc} = \frac{\mathcal{R}T}{4\mathcal{F}} \ln(p_{O_2(ca)}^{bulk}/p_{O_2(an)}^{tpb})$				unit cell	(4.40e)
Assumptions and Remarks					
<ul style="list-style-type: none"> i. It appears that in their model the electrochemical reactions were also assumed to occur at the anode/electrolyte interface (<i>i.e.</i> heterogeneous reactions are modeled through boundary conditions). ii. According to the authors, concentration polarization was calculated using Eq. (4.40e) for “half of the one repeating unit in the center part of the one-cell stack” (see “Fig. 1” in their paper). iii. The cell operating temperature in the model was set to 750 °C and fuel utilization to 85%. iv. In Eq. (4.40e) $p_{O_2(ca)}^{bulk}$ is the partial pressure of O_2 in the bulk of air stream, and $p_{O_2(an)}^{tpb}$ is the partial pressure of oxygen at electrolyte/anode interface. Equation (4.40e) appears to be based on Wagner equation for the electromotive force of a galvanic cell, which has a mixed ionic-electronic conductor^[69]. v. According to the authors, the experimentally measured concentration polarization (used for comparison purposes) was the average value over the anode (integral value over its length and thickness). 					

Yakabe and coauthors have used Eq. (4.40a) as a statement of “Darcy’s Law”, however its role in the actual modeling scheme is not clear, in the sense that this equation requires additional information (*e.g.*, boundary value information, prescribed values within the physical domain, other sub-constitutive equations, and so forth) in order to have complete physical significance. As it is, one has both the pressure gradient ∇p and superficial velocity u_s as unknown values. For example, a possible coupling possibility between modeling equations would be

$$\vec{N}_k = -C_g D_k^{\text{eff}} \nabla y_k + C_g y_k \vec{u}_s \quad (4.41)$$

Even though often used in the literature, Eq. (4.41) is not strictly correct in the presence of Knudsen or “frictional” flow^[211, 284]. Moreover, this formulation can lead to serious inconsistencies concerning the velocity (or rather, inertial) frame of reference. Equations (4.40b) and (4.40d) also present some problems. The former is a known result from DGM valid for isobaric counter-diffusion (hence, in this case the total pressure should be strictly uniform). Thus, it is not clear in which way the authors had intended to match this equation with “Darcy’s Law”, which considers the total pressure to vary spatially within the porous electrode. Equation (4.40d) possesses, on the other hand, problems to enforce mass conservativity because it applies a non-conservative form of diffusive fluxes^[211, 292, 303]. Finally, the use of Eq. (4.40e) to quantify the concentration polarization is at least controversial to whether it can be used to evaluate concentration losses directly. This equation really expresses the total EMF of the SOFC as expressed by, say, the Wagner equation, in that the SOFC is considered to be an

oxygen concentration cell^[109]. Yakabe and coauthors, in order to understand the effects of the gas composition and anode structure on the concentration polarization, they have compared the calculated concentration polarizations η_{conc} to that of a reference case $\eta_{conc,0}$ (see Fig. 4.4), where $\eta_{conc,0}$ is the concentration polarization at the ratio $y_{H_2}/(y_{H_2} + y_{H_2O}) = 0.8$ for a gas mixture present in the fuel channel (ternary H_2 - H_2O - Ar system). That is, in order to keep the open-circuit voltage constant, the ratio y_{H_2}/y_{H_2O} was fixed at 0.8/0.2, and the H_2 concentration in the fuel channel was modified by diluting H_2/H_2O with Ar .

$$\begin{aligned} \eta_{conc} - \eta_{conc,0} &= (E_{OCV} - E_{cell})_c - (E_{OCV} - E_{cell})_0 = \\ &= \left[\frac{RT}{2F} \ln \left(\frac{y_{H_2} y_{O_2}^{1/2}}{y_{H_2O}} \right) \right]_{c,bulk} - \left[\frac{RT}{2F} \ln \left(\frac{y_{H_2} y_{O_2}^{1/2}}{y_{H_2O}} \right) \right]_{0,bulk} + \frac{RT}{4F} \ln \left(p_{O_2(ca)}^{bulk} / p_{O_2(an)}^{tpb} \right)_c + \\ &\quad - \frac{RT}{4F} \ln \left(p_{O_2(ca)}^{bulk} / p_{O_2(an)}^{tpb} \right)_0 \end{aligned} \quad (4.42)$$

If, in the bulk of gas channels, $y_{H_2}/y_{H_2O} = 4 = \text{constant}$ and also $y_{O_2,c} = y_{O_2,0}$, then

$$\Rightarrow \eta_{conc} - \eta_{conc,0} = \frac{RT}{4F} \ln \left(p_{O_2(an),0}^{tpb} / p_{O_2(an),c}^{tpb} \right)$$

Thus, one sees that everything comes down to obtaining values of $p_{O_2(an)}^{tpb}$. However, Yakabe *et al.* have not made available the information on how $p_{O_2(an)}^{tpb}$ would have been theoretically calculated nor supposedly measured (in their paper, the authors compare the calculated concentration polarizations for the H_2 - H_2O - Ar system with experimentally measured values). Furthermore, in Eq. (4.42) they must have assumed that other voltage losses (e.g., ohmic and activation polarizations), under the same net current density, remain invariant with respect to the dilution of H_2/H_2O with Ar (effectively, to a reduction in the concentrations of H_2 and H_2O).

Figure 4.4: comparison of the measured and the calculated concentration polarization in a H_2 - H_2O - Ar ternary system. The open symbols and closed symbols denote the measured and the calculated results, respectively (figure reproduced from [286]). In their work, the authors have also made an analysis for the case of CO - CO_2 system.

One can only speculate that what they actually did was only to measure E_{cell} in conditions of distinct compositions and then compare results. In another study, Suwanwarangkul *et al.*^[270] made use of the experimental values from Yakabe *et al.* in order to compare different mass transfer models in SOFCs, but applying the usual definition of η_{conc} , e.g. according to Eq. (2.37).

4.5.2.3 Ackmann *et al.*

Ackmann *et al.*^[293] have presented a two-dimensional mathematical model to evaluate the diffusive mass transport in the porous structure of thick planar substrates, which are typically found in anode-supported SOFCs, using the MTPM⁷. Their aim was to examine operation conditions and the effect of the substrate structural parameters on the cell performance, for the case of SOFCs running under methane steam reforming and water-gas-shift reactions. To justify this study, the authors have noted that, in thicker anodic substrates (1.5 mm thick, in their simulations), there can be severe diffusional limitations, which, as a consequence, might lead to a spatial separation of reforming and electrochemical reactions, the latter being confined to a very thin region near the anode/electrolyte interface (as discussed in §2.3.3).

These authors claim that their MTPM implementation has several advantages over that of Yakabe *et al.*^[286] who used the parallel pore model (PPM). Among the claims, they state that in the MTPM both the permeability and diffusion coefficients are calculated from structural parameters of real porous materials, all of which can be determined directly by permeation and diffusion experiments in Wicke-Kallenbach cells. While it is eminently true that the mentioned structural parameters (e.g., tortuosity, porosity, and pore radii) can indeed be experimentally measured with support of MTPM, accepting such statement as an advantage is a flagrant misrepresentation. Firstly, because these parameters can also be measured using diffusion experiments in porous solids with the aid of PPM (there is a wealthy number of examples where this has been done^[287, 294, 289, 290, 213]). Secondly, because in their physical substance both MTPM and PPM are "two sides of the same coin", that is, they are really modified Maxwell-Stefan models with their roots on the derivations due to Mason and Evans^[291, 63], even sharing the same flaws and misleading definition of fluxes. Except for nomenclature personalisms (e.g., the structural factor ψ_{str} in the MTPM) and the constitutive Eq. [4.43g], their differences are immaterial, objectively speaking.

⁷ They implemented their model in the proprietary CFD code ANSYS Fluent™.

Table 4.4: Macro-homogeneous model from Ackmann *et al.* [293]

Governing Equations															
$\frac{\psi_{str}}{\mathcal{R} T} \frac{\partial(y_k p)}{\partial t} = -\nabla \cdot \tilde{\mathbf{N}}_k + \dot{S}_{v,y_k} \quad (\text{where } \psi_{str} = \varepsilon/\tau^2)$ <p style="text-align: center;">for $k = O_2, N_2$ in cathode for $k = H_2, H_2O, CO, CO_2, CH_4$ in anode</p>		in anode and cathode substrates	(4.43a)												
Constitutive Equations and Parameters															
$\tilde{\mathbf{N}}_k = \tilde{\mathbf{N}}_k^{diff} + \tilde{\mathbf{N}}_k^{perm}$		in anode and cathode substrates	(4.43b)												
$\frac{\tilde{\mathbf{N}}_k^{diff}}{D_k^{Kn,eff}} + \sum_{j \in \mathcal{N}_{gas}} \frac{y_j \tilde{\mathbf{N}}_k^{diff} - y_k \tilde{\mathbf{N}}_j^{diff}}{D_{k,j}^{eff}} = -C_g \nabla y_k$ <p style="text-align: center;">for $\mathcal{N}_{gas} = \{O_2, N_2\}$ in cathode for $\mathcal{N}_{gas} = \{H_2, H_2O, CO, CO_2, CH_4\}$ in anode</p>		in anode and cathode substrates	(4.43c)												
$D_k^{Kn,eff} = \psi_{str} \langle r_p \rangle \frac{2}{3} \left(\frac{8 \mathcal{R} T}{\pi M_k} \right)^{1/2}$		in anode and cathode substrates	(4.43d)												
$D_{k,j}^{eff} = \psi_{str} D_{k,j}$		in anode and cathode substrates	(4.43e)												
The binary gas diffusion coefficient $D_{k,j}$ is calculated using a standard Chapman–Enskog theory ^[263] .		in anode and cathode substrates	-												
$\tilde{\mathbf{N}}_k^{perm} = -\frac{B''_{MTPM,k}}{\mathcal{R} T} \nabla p$		in anode and cathode substrates	(4.43f)												
The permeability coefficient $B''_{MTPM,k}$ was determined by (see [281])															
$B''_{MTPM,k} = D_k^{Kn,eff} \left(\frac{Kn_k + M_{\Delta n,k} \pi/4}{1 + Kn_k} \right) + \frac{\langle r_p^2 \rangle \psi_{str} p}{8 \mu_m}$		in anode and cathode substrate	(4.43g)												
	<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th><th>$\psi_{str} (-)$</th><th>$\langle r_p \rangle (m)$</th><th>$\langle r_p^2 \rangle (m^2)$</th></tr> </thead> <tbody> <tr> <td>anode substrate</td><td>0.156</td><td>1.07×10^{-6}</td><td>3.8×10^{-13}</td></tr> <tr> <td>cathode substrate</td><td>0.037</td><td>2.34×10^{-6}</td><td>8.6×10^{-13}</td></tr> </tbody> </table>		$\psi_{str} (-)$	$\langle r_p \rangle (m)$	$\langle r_p^2 \rangle (m^2)$	anode substrate	0.156	1.07×10^{-6}	3.8×10^{-13}	cathode substrate	0.037	2.34×10^{-6}	8.6×10^{-13}		
	$\psi_{str} (-)$	$\langle r_p \rangle (m)$	$\langle r_p^2 \rangle (m^2)$												
anode substrate	0.156	1.07×10^{-6}	3.8×10^{-13}												
cathode substrate	0.037	2.34×10^{-6}	8.6×10^{-13}												
Source Terms															
$\dot{S}_{v,y_k} = \begin{cases} v_{k,el(O_2)} \dot{S}_{el(O_2)} & , \text{ in cathode substrate} \\ v_{k,sh} \dot{S}_{sh} + v_{k,re} \dot{S}_{re} + v_{k,el(H_2)} \dot{S}_{el(H_2)} + v_{k,el(CO)} \dot{S}_{el(CO)} & , \text{ in anode substrate} \end{cases}$			(4.43h)												
Assumptions and Remarks															
<ul style="list-style-type: none"> i. The cell operating temperature in the model was set to 700 °C and cell voltage to 0.7 V. Anode and cathode substrate thicknesses were 1.5×10^{-3} m and 6×10^{-5} m, respectively. ii. The MTPM is based on the assumption that the structure of the porous medium is isotropic. The porous nature of the medium is represented by three structural parameters: ψ_{str} the ratio of porosity ε to tortuosity τ^2; $\langle r_p \rangle$ the mean value of pore radii; and $\langle r_p^2 \rangle$ the mean value of squared pore radii. iii. Note the mistake on the LHS of Eq. (4.40a): porosity should be multiplying these terms, and not ψ_{str}. iv. Equation (4.43c) (a modified Maxwell-Stefan equation) is assumed to be valid in the transition region of Knudsen numbers (Kn_k), wherein both effects from free molecular diffusion (“Knudsen diffusion”) and hydrodynamic (“bulk”) diffusion are considered, depending on, <i>e.g.</i>, the length scale of the pores. The authors have not defined how Kn_k is to be evaluated based on this length scale (see [281]). 															

CONTINUATION OF TABLE 4.4	
Assumptions and Remarks	
v.	In Eq. (4.43f), the permeation flux density is described by Darcy's Law. This formulation also has inconsistencies concerning the velocity frame of reference (see [211, 221]).
vi.	In the derivation of Eq. (4.43g) there are implied assumptions regarding the rarified aspects of the flow and considerations on the pore geometry (see [281]). Apparently, this equation has a serious error in the last term of RHS, which is unbounded upon summation over all k gas species. Actually however, the error lies in the expression of Eq. (4.43f), from which the mole fraction (y_k) of species k is missing, that is, the equation should have been written as $\vec{N}_k^{\text{perm}} = -y_k B''_{MTPM,k}/(\mathcal{RT}) \nabla p$.
vii.	In Eq. (4.43h), the terms $\dot{s}_{el(O_2)}$, $\dot{s}_{el(H_2)}$, and $\dot{s}_{el(CO)}$ are the rates of reaction due to electrochemical reduction of oxygen, oxidation of hydrogen, and oxidation of carbon monoxide, respectively. The model for the evaluation of these reaction rates was neither included nor described by Ackmann and coauthors ^[293] ; instead these authors only mention that an “equivalent circuit model” was employed.

4.5.2.4 Zhu, Kee, Goodwin, Janardhanan, Deutschman, and Coauthors

A prominent framework of macro-homogeneous models for SOFC porous electrodes has been developed by H. Zhu and R. Kee (Colorado School of Mines), in cooperation with V. Janardhanan and O. Deutschman (Karlsruhe Institute of Technology), and with D. Goodwin (Caltech). Their work comprehends a wide range of topics, including: models for heterogeneous chemistry (e.g., direct internal reforming of primary fuels in SOFC anodes); quasi-elementary electrochemistry models (e.g., modified Butler-Volmer equations based on elementary, single-step reactions), multicomponent mass transport models, constitutive equations to “predict” properties of composite electrodes, among others. In the specific case of gas-phase mass transfer modeling, these authors are, beyond a doubt, advocates of the Dusty Gas Model (GDM). Part of their published works will now be presented and succinctly discussed.

In one of their first papers, Zhu and Kee^[138] have furnished the basic theoretical formulation to be used by mathematical models in order to represent the PEN of SOFC systems, thereby allowing the analysis of the effects of various cell polarizations. A peculiar feature of this work was the proposition of an “abstract nomenclature” for chemical reactions and chemical species, so to maintain generality in the modeling of arbitrary gas mixtures on the anode and cathode sides of the PEN. This nomenclature is not novel in the chemical process modeling literature (more precisely, in the simulation of chemical kinetic systems obeying the “law of mass action”); this level of abstract nomenclature is often implemented in numerical codes such as CHEMKIN software^[139]. In the same work^[138], the concentration polarization (e.g., concentration gradients stemming from the transport/reaction of gaseous species within porous electrodes) was evaluated with support from the DGM. A summary of this model, as applied by Zhu and Kee, is presented in Table 4.5.

Table 4.5: Macro-homogeneous model from Zhu and Kee [138].

Constitutive Equations and Parameters		
$-\nabla C_k = \sum_{j \neq k} \frac{C_j \vec{N}_k - C_k \vec{N}_j}{C_g D_{k,j}^{\text{eff}}} + \frac{\vec{N}_k}{D_k^{Kn,\text{eff}}} + \frac{C_k B}{\mu_m D_k^{Kn,\text{eff}}} \nabla p$	in porous electrodes	(4.44a)
$D_k^{Kn,\text{eff}} = \frac{\varepsilon}{\tau^2} \bar{r}_p \frac{4}{3} \left(\frac{8 \mathcal{R}T}{\pi M_k} \right)^{1/2}$	in porous electrodes	(4.44b)
$D_{k,j}^{\text{eff}} = \frac{\varepsilon}{\tau^2} D_{k,j}$	in porous electrodes	(4.44c)
The binary gas diffusion coefficient $D_{k,j}$ is calculated using a standard Chapman–Enskog theory ^[263] .	in porous electrodes	-
The permeability coefficient B was determined by the Kozeny–Carman relationship	in porous electrodes	(4.44d)
$B = \frac{\varepsilon^3 \bar{d}_p^2}{72 \tau^2 (1 - \varepsilon)^2}$	in porous electrodes	(4.44d)
$-\nabla p = \frac{\sum_k (\vec{N}_k / D_k^{Kn,\text{eff}})}{1/(\mathcal{R}T) + B/\mu \sum_k (C_k / D_k^{Kn,\text{eff}})}$	in porous electrodes	(4.44e)
Interface Conditions (“Internal Boundary Conditions”)		
$\vec{N}_{k,an} \cdot \vec{n} = (v'_{fu,k} - v''_{fu,k}) \frac{i}{z_e \mathcal{F}} \quad , \text{ at anode/electrolyte interface}$		(4.44f)
$\vec{N}_{k,ca} \cdot \vec{n} = (v'_{ox,k} - v''_{ox,k}) \frac{i}{z_e \mathcal{F}} \quad , \text{ at cathode/electrolyte interface}$		(4.44g)
Assumptions and Remarks		
<p>i. The electrochemical reactions are assumed to occur at the anode/electrolyte and cathode/electrolyte interfaces (<i>i.e.</i> heterogeneous reactions are modeled through boundary conditions). At these interfaces, the total molar flux is related to the electric current by Faraday's law, as per Eq. (4.44f) and (4.44g).</p> <p>ii. The total molar flux is taken as zero for any inert species that does not participate in the electrochemical reactions (<i>e.g.</i>, nitrogen in the cathode).</p> <p>iii. The main DGM equation, Eq. (4.44a), expresses an implicit relationship among the molar concentrations, molar fluxes, concentrations gradients, and the pressure gradient. In this equation $C_g = p/(\mathcal{R}T)$ is the total molar concentration and μ_m is a “mixture viscosity”, which depends on the mixture composition and temperature.</p> <p>iv. Note that in Eq. (4.40b), differently from Eq. (4.40c) and (4.43d), the factor 4/3 appears. It is not clear whether this difference is related or not to some assumption concerning an extra “correction” due to, <i>e.g.</i>, the accommodation coefficient of gas molecules on wall surfaces^[295]. The canonical definition of the diffusivity for Knudsen flow is obtained from the self-diffusion coefficient derived from the kinetic theory of gases^[161], which gives $D^{Kn} = d_p \bar{u}_T/3$, where $\bar{u}_T$ is the mean thermal velocity of the gas. Thus, $D^{Kn} = (2/3) \bar{r}_p [8 \mathcal{R}T/(\pi M_k)]^{1/2}$.</p> <p>v. The Kozeny–Carman relation given by Eq. (4.44d) assumes (<i>i.e.</i>, idealizes) that the porous layer is formed by closely packed spherical particles^[49] with diameter $\bar{d}_p$.</p>		

CONTINUATION OF TABLE 4.5

- vi. In order to determine the pressure gradient term, Eq. (4.44e) is used. This expression originates from the summation of Eq. (4.44a) over all species k , and also recognizing that the summation of the first term on the RHS vanishes exactly. As electrolyte interface concentrations are initially not known, an iterative procedure is employed to evaluate the pressure gradient, by first assuming an initial guess for the concentrations " C_k ". Subsequently, according to the authors, the concentrations " C_k " in the denominator of Eq. (4.44e) are then evaluated either with values taken at the gas channel interface or at the electrolyte interface, depending on the direction of the net molar flux $\sum_k \vec{N}_k$. If this flux is toward the electrolyte, then " C_k " are taken as the channel concentrations. Conversely, when the net flux is toward the channel, these concentrations are evaluated at the electrolyte interface. Once the pressure gradient has been determined, concentration gradients can now be obtained from Eq. (4.44a). Zhu and Kee^[138] propose to assume linear profiles of pressure and concentrations along the electrode thickness, thereby simplifying the analysis. Thus, by assuming linear concentration profiles and a known layer thickness, concentration gradients are evaluated and a new estimate for the concentrations at the TPB can be found. With new estimated gas concentrations, a new pressure gradient can be calculated. The iteration proceeds until satisfactory convergence is achieved.

In a next paper, Zhu, Kee, and coauthors^[83] have extended their previous computational framework for the modeling of chemically reacting flows in anode-supported SOFCs, considering the possibility of internal reforming of hydrocarbon fuels. The framework now incorporates the capability to represent elementary heterogeneous chemical kinetics in the form of multistep reaction mechanisms (mean-field approximation with mass-action kinetics). The charge-transfer chemistry is modeled through modified BVEs derived from elementary reactions, but assuming a single rate-limiting step. Again, concentration polarization is accounted for by solving the mass transport in the porous electrodes using the DGM. To illustrate an application for their framework, they chose a planar SOFC in which the fuel channel had a co-flowing architecture ("plug flow" approximation in the mean flow direction). However, the authors state that their theory is independent of this particular geometry. The internal reforming model was exemplified through the case of CH_4 steam reforming on Ni -based catalysts, whose reaction mechanism consisted of 42 reversible reactions, involving 6 gas-phase and 12 surface-adsorbed species.

Table 4.6: Macro-homogeneous model from Zhu et al. [83].

CONTINUATION OF TABLE 4.6				
Governing Equations				
$\frac{d(\rho_g x_k u)}{dx} = \frac{\mathcal{P}_e}{\mathcal{A}_c} \tilde{N}_k M_k, \text{ for } k = H_2, H_2O, CO, CO_2, CH_4$	in fuel channel	(4.45a)		
$\frac{d(\rho_g u)}{dx} = \frac{\mathcal{P}_e}{\mathcal{A}_c} \sum_{k \in \mathcal{N}_{gas}} \tilde{N}_k M_k$ for $\mathcal{N}_{gas} = \{H_2, H_2O, CO, CO_2, CH_4\}$	in fuel channel	(4.45b)		
$\frac{d\tilde{N}_k}{dz} = a_s \dot{S}_{s,C_k}$	in porous anode	(4.45c)		
Constitutive Equations and Parameters				
$\rho_g = \frac{p}{\mathcal{R}T} \frac{1}{\sum_k x_k / M_k} = \frac{p \bar{M}_n}{\mathcal{R}T}$	in fuel channel	(4.45d)		
$-\frac{dC_k}{dz} = \sum_{j \neq k} \frac{C_j \vec{\tilde{N}}_k - C_k \vec{\tilde{N}}_j}{C_T D_{k,j}^{eff}} + \frac{\vec{\tilde{N}}_k}{D_k^{Kn,eff}} + \frac{C_k B}{\mu_m D_k^{Kn,eff}} \nabla_z p$	in porous anode	(4.45e)		
$D_k^{Kn,eff} = \frac{\varepsilon}{\tau^2} \bar{r}_p \frac{4}{3} \left(\frac{8 \mathcal{R}T}{\pi M_k} \right)^{1/2}$	in porous anode	(4.45f)		
$D_{k,j}^{eff} = \frac{\varepsilon}{\tau^2} D_{k,j}$	in porous anode	(4.45g)		
The binary gas diffusion coefficient $D_{k,j}$ is calculated using a standard Chapman–Enskog theory ^[263] .	in porous anode	-		
The permeability coefficient B was determined by the Kozeny–Carman relationship:				
$B = \frac{\varepsilon^3 \bar{d}_p^2}{72 \tau^2 (1 - \varepsilon)^2}$	in porous anode	(4.45h)		
$\tilde{N}_k = - \sum_{j=1}^{\mathcal{N}_{gas}} \left(D_{k,j}^{DGM} \frac{dC_k}{dz} \right) - \left[\sum_{j=1}^{\mathcal{N}_{gas}} \left(D_{k,j}^{DGM} \frac{C_k}{D_k^{Kn,eff}} \right) \right] \frac{B}{\mu_m} \nabla_z p$	in porous anode	(4.45i)		
$[\mathbf{D}^{DGM}] = \vec{\vec{D}}^{DGM} = [\mathbf{H}^{-1}]$	in porous anode	(4.45j)		
Where the elements of the $[\mathbf{H}]$ matrix are				
$h_{kl} = \left(\frac{1}{D_k^{Kn,eff}} + \sum_{j \neq k} \frac{C_j}{D_{k,j}^{eff}} \right) \delta_{kl} + (1 - \delta_{kl}) \frac{C_k}{D_{k,l}^{eff}}$	in porous anode	(4.45k)		
Layer thickness (μm): 1220	Average pore radius $\bar{r}_p$ (μm): 0.5			
Porosity ε (%): 35	Average pore diameter $\bar{d}_p$ (μm): 2.5	in porous anode		-
Tortuosity factor τ^2 (-): 2.5	Specific catalyst area a_s (cm^{-1}): 1080			
Interface Conditions (“Internal Boundary Conditions”)				
$\vec{\tilde{N}}_k \cdot \vec{n} = v_k \frac{i}{z_e \mathcal{F}}, \text{ at anode/electrolyte interface}$		(4.45l)		
At the anode/channel interface, the gas-phase species composition is required to match that in the fuel channel, at every axial position x .		-		

CONTINUATION OF TABLE 4.6

Source Terms

$$\dot{S}_{S,C_k} = \sum_i^{N_{reac}} v_{k,i} \dot{q}_i \quad \text{in porous anode} \quad (4.45m)$$

Assumptions and Remarks

- i. Part of notes provided for the case of Zhu and Kee^[138] in Table 4.5 applies here as well.
- ii. In Eq. (4.45a) and (4.45b) the channel geometry is characterized by the cross-sectional area $\mathcal{A}_c$ and the perimeter $\mathcal{P}_e$ associated with the electrochemically active PEN. According to the Figure above, $\mathcal{P}_e$ includes the width of the gas channel plus the width of the electrode. Here, $\tilde{N}_k$ is the total molar flux of the k -th species evaluated at the channel/anode interface, *i.e.*, $\tilde{N}_k = \tilde{N}_k(z = 0)$.
- iii. To justify the PFR model for the fuel channel, Eq. (4.45a) and (4.45b), the authors consider the gas flow therein to be one-dimensional and laminar. They state that this is a good approximation because fuel channels typically have diameters less than a centimeter and mean velocities of less than 100 cm/s. Thus, Reynolds number is expected to be on the order of ≤ 100 . Hence the flow is highly viscous and a fully developed velocity profile is established very near the channel entrance (see §§4.10 for discussion).
- iv. In the fuel channel, the authors also neglect variations of the gas composition transverse to the flow direction, assuming that “rapid diffusion of species across the channel width homogenizes the composition transverse to the flow”. That is, they disregard any mass transfer resistance in the wall direction or, which is the same, the flow has no “mass boundary layer” (see §§4.10 for discussion).
- v. It seems to be a problem with the solution of fuel channel, if one takes into consideration the statement made by the authors in that the velocity u is free to vary in the channel. In this case, there are more unknowns than equations, *i.e.* the problem is under-determined (see note “i” in Table 4.8).
- vi. In the steady-state description of molar fluxes, Eq. (4.45c), $\dot{S}_{S,C_k}$ is net production rate (per unit of active area) due to heterogeneous chemistry and a_s is the active catalyst area available for surface reaction per unit volume. The authors state that as the electrode thickness is much smaller than its length, gradients are primarily in the z direction (transport through the electrode is taken as approximately 1D).
- vii. This molar production rate $\dot{S}_{S,C_k}$, Eq. (4.45m), is evaluated using the proposed heterogeneous reaction mechanism in Zhu *et al.*^[83]. Since this mechanism is formulated in terms of elementary reactions on the catalyst surface, the reaction rates depend both on the concentrations of the gaseous reactants and on the coverages of the surface species, the latter represented by surface sites and adsorbates. Since these coverages are not known *a priori*, they must be determined as part of the solution process. However, the way in that this is accomplished is not indicated in their paper. It is likely that a “pseudo-transient” conservation equation for surface species was added to the set of equations.
- viii. The authors assume that surface species are effectively immobile on length scales larger than an individual catalyst particle. Thus, at steady state, values of surface coverage must be such that the net production rate due to chemistry is zero for every surface species (*i.e.*, $\dot{S}_{S,C_k} = 0$ when k is a surface species). Evidently, this is a corollary assumption within the mean-field approximation, but it does not mean it is a good approximation for the real problem being solved^[296, 132, 55].
- ix. It is important to mention that the authors assume that the DGM can be used over the full range of Knudsen numbers (Kn): from values much larger than 1 (when molecule-wall collisions should dominate), to values much less than 1 (when molecule-molecule collisions should dominate).
- x. Differently from their previous work, here the authors propose a direct representation of $\tilde{N}_k$ as given by Eq. (4.45i), so to facilitate (or make more convenient) the solution of the system of equations, Eq. (4.45e), which must be solved simultaneously for each of the k components of $[\mathbf{N}]$. In this representation, the DGM diffusion coefficients (*i.e.*, the second-order tensor $\mathbf{D}^{DGM}$) are represented as a matrix inverse $[\mathbf{H}^{-1}]$, a format often applied in the literature for Maxwell-Stefan models^[64, 185, 297].

On what concerns concentration losses, specifically, in their subsequent works^[31, 298, 299, 300] Janardhanan, Deutschmann, and coworkers adopt the same modeling framework as described in the foregoing, though with some noteworthy differences. Some of them, which will be presented in the next pages, deserve attention in that they can help to understand a number of artifacts introduced by mathematical models in counterpoint to experimental observation. The authors applied^[31] their “generic” computational framework to study the specific case of an anode-supported button cell running on humidified CH_4 (3% H_2O and air as the oxidant), under direct internal reforming conditions. Essentially, what differentiates this work from the previous ones is the use of standard finite-volume CFD techniques⁸ for solving mass transfer and flow-field (two-dimensional) equations in the fuel channel and porous electrode. Table 4.7 summarizes the modeling equations that are different in comparison to those of their previous work (see Table 4.6).

Table 4.7: Macro-homogeneous model from Janardhanan and Deutschmann [31].

Governing Equations		
$\nabla \cdot (\rho_g \vec{V}) = \dot{S}_{V,m}$	(unspecified)	(4.46a)
$\nabla \cdot (\rho_g \vec{V} \vec{V}) = -\nabla p - \frac{2}{3} \nabla \cdot (\mu_m \nabla \vec{V}) + \nabla \cdot [\mu_m (\nabla \vec{V} + (\nabla \vec{V})^T)] + \vec{F}_D$	(unspecified)	(4.46b)
$\nabla \cdot (\rho_g x_k \vec{V}) = -\nabla \cdot \vec{N}_k + M_k a_s \dot{S}_{S,C_k}$	(unspecified)	(4.46c)
Constitutive Equations		
$\vec{N}_k = M_k \vec{N}_k$ see also Eq. (4.45i)	in porous anode	(4.46d)
$\vec{F}_D = \begin{cases} -(\mu_m/B) \vec{V} & , \text{porous anode} \\ 0 & , \text{elsewhere} \end{cases}$		(4.46e)
Source Terms		
$\dot{S}_{V,m} = \begin{cases} \sum_{k \in \mathcal{N}_{gas}} M_k a_s \dot{S}_{S,C_k} & , \text{only at the TPBs (electrochemical reactions)} \\ 0 & , \text{elsewhere} \end{cases}$		(4.46f)
Assumptions and Remarks		
<p>i. The designation “unspecified” points out the fact that in this paper there was no explicit indication that a given equation is to be employed in a specific domain (e.g., fuel channel and/or electrode). This information is implied solely by the form of the equation, from which ambiguity or model uncertainty might arise. For instance, the total velocity ($\vec{V}$) vector has different meanings when in the context of pure fluid or porous electrode: in the latter case, it must represent a macroscopic superficial velocity and not the “true velocity” of gas flow within the voids of the porous medium. Otherwise, the porosity (ε) should have been used to make the necessary differentiation.</p>		

⁸ They have implemented their framework (Table 4.6) in the CFD code ANSYS Fluent™.

CONTINUATION OF TABLE 4.7

- ii. Equation (4.46a) represents the continuity of the total mass of the system, in a given bounded domain. In principle, the source term $\dot{S}_{v,m}$ in this equation should be always zero (everywhere) to ensure mass conservation. However, by inspecting Eq. (4.46f) one verifies that it can be nonzero at the TPBs, wherein electrochemical reactions are taking place. In this case, therefore, $\dot{S}_{v,m}$ really represents what is sometimes called a “spurious source term”, which can arise as a result of the incomplete (no-rigorous) description of the boundary value problem. Heterogeneous chemical reactions, on the physical scale of description of Eq. (4.46f), are (usually) taken into account through boundary conditions prescribed at the surfaces (“walls”) of the domain. However, if, for example, the problem’s dimensionality excludes any description of phenomena along the spatial coordinate parallel to wall direction, then these phenomena may be evaluated through ad hoc “corrections”, *i.e.*, source terms in the case of Eq. (4.46f). Thus, heterogeneous reactions are represented as “pseudo-homogeneous reactions” because $\dot{S}_{v,m}$ is incorporated in the homogenous (continuum) description of the domain. Nonetheless, in the particular case of Janardhanan and Deutschmann model in [31], these authors considered a two-dimensional description of the problem (that includes the spatial coordinate parallel to wall direction), yet, oddly enough, they have kept the spurious source term.
- iii. Equation (4.46b) represents momentum balances (linear momentum “conservation” for a dissipative system). When also taking into consideration Eq. (4.46e) for electrode domains, it resembles the “Brinkman equation”^[54, 47]. A few remarks about this equation⁹ are given here with the hope that they might serve for a better understanding of this modeling approach adopted by the authors.
- First, it is noted that the same remark made in “i” is still pertinent, that is, the absence of the porosity factor to clearly indicate that this equation refers to a porous domain.
 - The inclusion of the term $\vec{F}_D$ entails the same assumptions of Darcy’s Law. In fact, Eq. (4.46b) simplifies to Darcy’s Law in the absence of meaningful stresses and for flows with sufficiently low Reynolds number. Appearance of field quantities (stresses) in a macroscale equation which describes the flow in porous media is an interesting (and important) discussion. However, it should be already mentioned that the consideration of such field quantities, as in Eq. (4.46b), is of doubtful physical significance.
 - Considering the continuity equation as given by Eq. (4.46a), the momentum Eq. (4.46b) is not strictly correct, because the “net mass source term” should have been added to it.
 - The “coefficient of dynamic viscosity” (μ_m) that multiplies the stresses in Eq. (4.46b) is not the same as the one that appears in Eq. (4.46e), for which the authors made no distinction. These coefficients are different for reasons related to both the scale dependence of gas viscosity in porous media and to rarefaction effects^[301, 302, 303, 199].
- iv. Equation (4.46c) is erroneous in the way it expresses material fluxes. If the pressure gradient is considered, DGM constitutive equations can only be written in terms of total fluxes ($\vec{N}_k$) and thus never in terms diffusive fluxes ($\vec{J}_k$). Therefore, it turns out that in Eq. (4.46c) there is the double counting of fluxes^[211]. That is, $\vec{N}_k = \rho_g x_k \vec{V} + \vec{J}_k$ and so $\nabla \cdot (\rho_g x_k \vec{V}) + \nabla \cdot \vec{N}_k = \nabla \cdot (2 \rho_g x_k \vec{V} + \vec{J}_k)$. The authors have made the misleading assumption that $\vec{N}_k$ can be taken as the diffusive flux in Eq. (4.46c) and Eq. (4.45i).

In another study, the author’s computational framework was again used to numerically investigate a planar SOFC under direct internal reforming conditions^[298], but at this time the authors have analyzed the influences of certain operating parameters on optimal cell operation and aspects related to heat transfer, such as: (i) the influence of the steam-to-carbon ratio of

⁹ For the fluid domain, on the other hand, this equation does not deserves special attention in this regard, as it is really the standard, steady-state “compressible” Navier-Stokes equation for the mean flow, written in the high Froude limit. There is, however, an “incorrect notation” concerning part of the non-deviatoric (“mean”) stress tensor in this equation: the second term on the RHS of Eq. (4.46b) should have been written as $-2/3 \nabla \cdot [\mu_m (\nabla \cdot \mathbf{V}) \mathbf{I}]$, where $\mathbf{I}$ is the second rank unit tensor. Or, alternatively, as $-2/3 \nabla(\mu_m \nabla \cdot \mathbf{V})$.

inlet fuel on the operating temperature and on the propensity to form carbonaceous solid deposits (within the anode); (ii) main differences between isothermal and adiabatic operational regimes; (iii) impact of fuel pre-reforming on cell performance, regarding the possibility to increase efficiency by the reutilization of waste heat. More recently^[300], the authors applied the same computational strategy as the above mentioned work to the analysis of mass and heat transport in SOFCs designed with a novel electrolyte material (proton-conducting electrolyte, in place of the more conventional design that uses an oxide ion-conducting material). Table 4.8 summarizes the modeling equations that are different in comparison to their previous works (tables 4.6 and 4.7).

Table 4.8: Macro-homogeneous model from Janardhanan <i>et al.</i> [298] & Menon <i>et al.</i> [300]			
Governing Equations			
$\frac{\partial(\rho_g u)}{\partial t} = -\frac{\partial(\rho_g u u)}{\partial x} + u \frac{\mathcal{P}_e}{\mathcal{A}_c} \sum_{k=1}^{N_{gas}} M_k \tilde{N}_k$	in fuel channel	(4.47a)	
$\frac{\partial(\varepsilon \rho_g x_k)}{\partial t} = -\frac{\partial(\tilde{N}_k M_k)}{\partial z} + M_k a_s \dot{S}_{S,C_k}$	in porous anode	(4.47b)	
$\frac{\partial(\varepsilon \rho_g)}{\partial t} = -\sum_{k=1}^{N_{gas}} \frac{\partial(\tilde{N}_k M_k)}{\partial z} + a_s \sum_{k=1}^{N_{gas}} M_k \dot{S}_{S,C_k}$	in porous anode	(4.47c)	
Constitutive Equations			
$D_k^{Kn,eff} = \frac{\varepsilon}{\tau^2} \bar{r}_p \frac{2}{3} \left(\frac{8 RT}{\pi M_k} \right)^{1/2}$	in porous anode	(4.47d)	
Assumptions and Remarks			
<ul style="list-style-type: none"> i. Now one sees that an additional momentum balance, Eq. (4.47a), was added to the system of equations. This axial momentum equation was absent in their previous works (see remark “v” in Table 4.6). A short discussion on the origin and validity of this equation will be made in APPENDIX A. In [298] there is a typographic error in this equation, in which the parameter $\mathcal{A}_c$ is missing. ii. The authors abandoned Eq. (4.46c) in detriment of Eq. (4.47b) to describe the species mass conservation, thus previous errors are no longer present (see remark “iv” in Table 4.7). iii. The additional time-dependent term in Eq. (4.47a), Eq. (4.47b), and (4.47c) is added for numerical purposes only (under-relaxation during the convergence steps), that is, at each axial position the transient system of equations is solved until a steady-state (converged) solution is obtained (see APPENDIX A). The use of this transient form of the equations now requires computing the total density (ρ_g) of the gas-phase within the porous structure. Thus, Eq. (4.47c) was incorporated to the set of equations (to match the number of unknowns of the problem). In this form, differently from Table 4.7, the porosity factor is now included. iv. In Eq. (4.47d), the Knudsen diffusivity formula was changed (corrected?) to use the “2/3” factor (see remark “iv” in Table 4.5). 			

In their later work^[304], Zhu, Kee, and coauthors chose an alternative approach (“modified Fickian diffusion model”) to that of DGM for studying the multidimensional flow behavior in button-cells. The aim of this study was to assess the validity of commonly made assumptions (e.g., uniform feed gas composition along the fuel channel/electrode interface) and their impact on the quantitative analysis and interpretation of button-cell experiments. For that the authors developed a three-dimensional CFD model of fluid, chemistry, and thermal transport flow (see Table 4.9). They also compared this “full” 3D model with often used one-dimensional models to pinpoint their differences when certain simplifying assumptions are violated. Particularly, some topics discussed by this paper will be examined in §§4.10.

Table 4.9: Macro-homogeneous model from Goldin *et al.* [304].

Governing Equations		
$\nabla \cdot (\rho_g \mathbf{V}) = 0$	in fuel channel and porous anode	(4.48a)
$\nabla \cdot (\rho_g x_k \mathbf{V}) = -\nabla \cdot \mathbf{J}_k$	in fuel channel	(4.48b)
$\nabla \cdot (\rho_g \mathbf{V}\mathbf{V}) = \nabla \cdot \left[\mu_m (\nabla \mathbf{V} + (\nabla \mathbf{V})^T) - \frac{2}{3} \mu_m (\nabla \cdot \mathbf{V}) \mathbf{I} \right] - \nabla p + \rho_g \mathbf{g}$	in fuel channel	(4.48c)
$\nabla \cdot (\rho_g x_k \mathbf{V}) = -\nabla \cdot \mathbf{J}_k + M_k a_s \dot{S}_{s,y_k}$	in porous anode	(4.48d)
$\nabla \cdot (\rho_g \mathbf{V}\mathbf{V}) = -\nabla p + \rho_g \mathbf{g} - \frac{\mu_m}{B} \mathbf{V}$	in porous anode	(4.48e)
Constitutive Equations		
$\mathbf{J}_k = -\rho_g D_{km} \nabla x_k$	in fuel channel	(4.48f)
$\mathbf{J}_k = -\rho_g D_k^{\text{eff}} \nabla x_k$	in porous anode	(4.48g)
$D_{km} = \frac{1 - y_k}{\sum_{j \neq k} \left(\frac{y_j}{D_{k,j}} \right)}$	in fuel channel and porous anode	(4.48h)
$\frac{1}{D_k^{\text{eff}}} = \frac{\tau^2}{\varepsilon} \left(\frac{1}{D_{km}} + \frac{1}{D_k^{Kn}} \right)$	in fuel channel and porous anode	(4.48i)
Assumptions and Remarks		
<ul style="list-style-type: none"> i. See notes provided in tables 4.4 (“vii”), 2.5 (“i”, “ii”), 2.6 (“vii”, “viii”), 2.7 (“i”, “iii”), and 2.8 (“iv”). ii. Differently from Eq. (4.46b), “effective viscous stresses” were neglected in Eq. (4.48e). Inertial effects and viscous drag were retained though. It is not clear if the buoyancy force was, in fact, taken into consideration during the actual numerical simulations (<i>i.e.</i>, if Richardson number is not vanishing small). iii. As also mentioned for the model of Yakabe <i>et al.</i>^[286], Eq. (4.48h) has problems to enforce mass conservation, because it applies a non-conservative form of diffusive fluxes^[305, 306, 292]. iv. Effective mixture-averaged diffusion coefficients were evaluated using the Bosanquet formula Eq. (4.46i). v. The applied definition of diffusive flux, Eq. (4.48f) and (4.48g), has issues related to the frame of reference, <i>e.g.</i>, these constitutive equations are not frame indifferent/invariant^[217, 218, 219]. 		

4.5.2.5 Yong, Haberman, and Todd

Yong, Haberman, and Todd applied new approaches for modeling fluid flow and mass transfer in SOFCs^[307, 292, 308], which included the development of a new theoretical model for gas-phase transport in porous electrodes, denominated as Cylindrical Pore Interpolation Model (CPIM). These authors have focused on the simulation of chemically reacting gas flows in the porous support structure of an integrated-planar SOFC (IP-SOFC), which is based on a cell design pioneered by Rolls-Royce (see Table 4.10 for an illustrative scheme of this design). This porous structure (a reactive anode support, in terms of its main functionality) is impregnated with the required catalysts for the steam reforming of methane.

Yong and Haberman have studied two simulation cases: one in which a pre-reformer module is employed^[308] and another in which it is not^[307]; however, in both cases, the electrochemical cell (*i.e.*, the SOFC) was not actually modeled, that is, electrochemical reactions were accounted for by prescribing fixed mass fluxes at the anode-electrolyte interface, which in their turn were calculated for a fixed, uniform electric current density. The reason for such oversimplification is, apparently, because the main interest in these studies was on the peculiarities of CH_4 reforming and WGS reactions. In the two case studies the authors employed two different mathematical models to simulate the mass transfer within the porous support structure (see tables 4.10 and 4.11). In their later work, which simulated the effect of a pre-reformer module^[308], they used the CPIM^[292].

Table 4.10: Macro-homogeneous model from Haberman and Yong [307].

<p style="text-align: center;">Three-dimensional representation of the simulation of a IP-SOFC</p>		
Governing Equations Coupled to Constitutive Equations (<i>i.e.</i>, Transport Equations)		
$-\nabla p = \frac{\mu_m \varepsilon}{B} \mathbf{V}_p$	in porous structure	(4.49a)
$-\nabla p = \frac{\mu_m \varepsilon}{B} \mathbf{V}_p - \nabla \cdot (\mu_m \nabla) \mathbf{V}_p$	in porous structure	(4.49b)

CONTINUATION OF TABLE 4.10

$Re_p = \frac{\rho_g \ \mathbf{V}_p\ \bar{d}_p}{\mu_m}$	in porous structure	(4.49c)
$\nabla \cdot (\rho_k \mathbf{V}_{p,k}) = \dot{S}_{\nabla, \rho_k}$	in porous structure	(4.49d)
Constitutive Equations and Parameters		
$\rho_k \mathbf{V}_{p,k} = \rho_k \mathbf{V}_p + \frac{\mathbf{J}_k}{\tau^2}$	in porous structure	(4.49e)
$\nabla y_k = \frac{\bar{M}_n}{\rho_g} \sum_{j=1}^N \left(\frac{\mathbf{J}_j y_k}{M_j D_{k,j}} - \frac{\mathbf{J}_k y_j}{M_k D_{k,j}} \right)$	in porous structure	(4.49f)
$[\nabla y] = -\frac{\bar{M}_n}{\rho_g} [\mathbf{D}^{MS}] [\mathbf{J}]$	in porous structure	(4.49g)
$D_{k,k}^{MS} = \frac{y_k}{M_N D_{k,N}} + \frac{1}{M_k} \sum_{\substack{j=1 \\ j \neq k}}^N \frac{y_j}{D_{k,j}}$	in porous structure	(4.49h)
$D_{k,j}^{MS} = -y_k \left(\frac{1}{M_j D_{k,j}} - \frac{1}{M_N D_{k,N}} \right)$	in porous structure	(4.49i)
$\mathbf{J}_N = -\sum_{j=1}^{N-1} \mathbf{J}_j$	in porous structure	(4.49j)
Porous structure thickness (μm): 1000		
Porosity ε (%): 50		
Tortuosity factor τ^2 (-): ? (not specified)	in porous structure	
Permeability coefficient B (m^2): 3.125×10^{-12}	$(MgAl_2O_4)$	
Average pore diameter $\bar{d}_p$ (μm): 10		
Assumptions and Remarks		
<p>i. Haberman and Yong developed an in-house CFD code for solving the (two-dimensional) set of governing equations. The authors stated to have used a finite-volume, time-marching method for structured grids. Thus, the I form of governing Eq. (4.49b) and (4.49d), as actually implemented in their numerical code, ought to have included a transient term to account for the numerical relaxation (time march).</p> <p>ii. The model for the macroscopic flow within the porous structure was again the empirical Darcy equation, Eq. (4.49a), which describes the balance between the force from the pressure gradient ∇p and the frictional resistance from the solid material. Here, however, Haberman and Yong decided to express this equation using the pore velocity vector $\vec{V}_p$, instead of the superficial velocity (volume flow rate per unit area through the porous structure) as has been done by the previous authors cited herein. This superficial velocity ($\vec{u}_s$) can be obtained by multiplying $\vec{V}_p$, the mean velocity within a pore (cross-section), by ε.</p> <p>iii. In this approach, Haberman and Yong decoupled "diffusive fluxes" from "convective fluxes", similarly to what have been presented in tables 4.3, 4.4, and 4.9. According to Eq. (4.49e), the flux vector of the k-th species, $\rho_k \vec{V}_{p,k}$, is defined as the sum of "convection and diffusion fluxes", where the mass-averaged pore velocity $\vec{V}_p$ is the velocity calculated from the Darcy Eq. (4.49a).</p>		

CONTINUATION OF TABLE 4.10

- iv. The authors included a definition for the Reynolds number, Eq. (4.49c), so to discuss the range of validity of Eq. (4.49a). They stated that this latter equation is valid for $Re_p < 1$. In their paper, the maximum value of Re_p was about 0.0001 and hence the use of Eq. (4.49a) would be well justified. Nevertheless, the Darcy equation can only describe the flow in the porous structure well away from the walls, *i.e.*, It cannot model a no-slip condition at a wall nor the resulting “boundary layers”¹⁰. Haberman and Yong provided an approximate theoretical analysis in order to estimate the likely magnitudes of these “boundary layers”. They have modified Eq. (4.49a) to allow calculation of the velocity boundary layers at the edges of the porous structure by adding the so-called “Brinkman” term to the Darcy equation, according to Eq. (4.49b). The normal stresses in this term were, however, ignored (see also note “iii-b” in Table 4.7).
- v. Diffusion mass fluxes $\vec{J}_k$ were derived from Maxwell–Stefan relations^[216, 65], Eq. (4.49f), which were written in matrix form, Eq. (4.49g), for the first $N - 1$ fluxes. Thus $[\nabla y]$ and $[\mathbf{J}]$ are matrices of size $(N - 1) \times 3$ (in a three-dimensional problem). The matrix $[\mathbf{D}^{MS}]$ is a square matrix of order $(N - 1)$. The first $N - 1$ diffusion fluxes are determined by inverting the matrix $[\mathbf{D}^{MS}]$. The N -th flux $\vec{J}_N$ is then found from the condition that the diffusive fluxes must sum to zero, Eq. (4.49j).
- vi. Their definition of diffusive flux, Eq. (4.49f), has problems related to the adopted frame of reference (see also note “v” in Table 4.9). The way it has been expressed (*i.e.*, using mole fraction gradients) is not coherent with the adoption of a mass-averaged velocity referential (see note “i” in Table 4.14).
- vii. In this work, the authors did not consider Knudsen “diffusion” in their mass transfer model.
- viii. Figure 4.6 shows the simulation results for the gas velocity vector $\vec{V}_p$ in the x – y plane. The variation of the y -direction velocity V_{py} is shown in Fig. 4.5a and the x -direction velocity V_{px} is shown in Fig. 4.5b. From these figures one verifies that a net mass flux enters the porous structure at the anode interface ($y = 1$ mm) and travels downward through the domain, “spreading” by a small amount in the x -direction. Within the boundary layer adjacent to the fuel channel ($y = 0$), V_{px} is of a similar magnitude as the variations at $y = 1$ mm.
- ix. Figure 4.5c shows the simulation results for the pressure distribution within the domain. The authors stated that the overall pressure gradient in the x -direction is brought about by the prescribed pressure drop in the fuel channel (note that neither modeling equations nor physical information were given for the simulation of the fuel channel in this paper, besides the short discussion made at the Appendix section therein). They also pointed out that in order to conserve mass, the pressure increases in the regions adjacent to each anode, where mass enters the system. This pressure rise results in a pressure gradient in the x -direction which causes the spreading of the flow in the x -direction at the anode edges.

Table 4.11: Macro-homogeneous model from Haberman and Yong [308].

Governing Equations Coupled to Constitutive Equations (*i.e.*, Transport Equations)

$$\frac{\varepsilon}{\tau^2} \frac{dp}{dz} = -\frac{1}{A_A} \sum_{k=1}^N M_k^{-1/2} \bar{N}_k, \quad \text{where} \quad \frac{1}{A_A} = \frac{1}{A_C} + \frac{1}{A_K} \quad \text{in porous structure} \quad (4.50a)$$

$$A_C = \frac{32 \mu_m}{\bar{d}_p^2 \rho_g} \frac{1}{\sum_k x_k M_k^{-1/2}} \quad \text{in porous structure} \quad (4.50b)$$

$$A_K = \frac{3}{\bar{d}_p} \left(\frac{\pi R T}{8} \right)^{1/2} \quad \text{in porous structure} \quad (4.50c)$$

¹⁰ Darcy equation cannot handle correctly situations in which Stefan velocities at wall are (substantially) different from those existing in the “bulk” of the homogenized porous medium. The same is true if “diffusion slip” phenomenon occurs in a significant way^[197, 196, 195].

CONTINUATION OF TABLE 4.11		
$\varepsilon \frac{\partial \rho_k}{\partial t} = -\frac{\partial \bar{N}_k}{\partial z} + \varepsilon \dot{S}_{v,\rho_k}$	in porous structure	(4.50d)
Constitutive Equations and Parameters		
$\frac{\varepsilon}{\tau^2} \frac{dx_k}{dz} = \frac{1}{\rho_g} \sum_{j=1}^N \left(\frac{\bar{N}_j x_k}{D_{j,k}^A} - \frac{\bar{N}_k x_j}{D_{k,j}^A} \right)$	in porous structure	(4.50e)
$\frac{1}{D_{k,j}^A} = \frac{1}{D_{k,j}} + \frac{1}{D_k^{Kn}}$	in porous structure	(4.50f)
$D_k^{Kn} = \bar{r}_p \frac{2}{3} \left(\frac{8 \mathcal{R}T}{\pi M_k} \right)^{1/2}$	in porous structure	(4.50g)
Porous structure thickness (μm): 1550 Porosity ε (%): 20 Tortuosity factor τ^2 (-): 2 Average pore diameter $\bar{d}_p$ (μm): 2	in porous structure (MgAl_2O_4)	
Assumptions and Remarks		
i. In this work, Haberman and Yong applied the CPIM theory ^[292] , thus abandoning most of their previous mathematical model.

Figure 4.5: field distributions within the porous structure: (a) y -direction velocity distribution; (b) x -direction velocity distribution; (c) and static pressure distribution (figure reproduced from [307]).

Figure 4.6: velocity vector $\vec{V}_p$ distribution within the porous structure of an IP-SOFC and in a region near the fuel channel interface (figure reproduced from [307]).

4.5.2.6 Jin, Xue, and Xie

Jin, Xue, and Xie developed CFD analyses (mainly for two-dimensional, axisymmetric computational domains) of multi-physicochemical processes in SOFCs and SOECs, including: direct internal reforming of CH_4 and H_2S in anode-supported cells^[309, 310]; electrochemical co-oxidation of H_2 and CO described through elementary reactions^[311, 309]; numerical assessment of the cell tolerance and failure resulting from delamination phenomenon^[312]; and reliability analysis of SOFCs wherein the coupling of chemical–mechanical phenomena develop due to the volumetric expansion of ceramic components, leading to the so-called chemical stresses^[313]. These authors have not used the same mathematical models of fluid flow and mass transfer throughout their works and important differences exist concerning the way in which concentration losses have been calculated. Tables 4.12, 4.13, 4.14, and 4.15 include relevant information for comparing these models.

Table 4.12: Macro-homogeneous model from Xie and Xue, [311].

Governing Equations Coupled to Constitutive Equations (*i.e.*, Transport Equations)

$\nabla \cdot \left[-\rho_g x_k \sum_j D_{j,k}^{\text{eff}} \left(\nabla y_j + (y_j - x_j) \frac{\nabla p}{p} \right) - D^T \frac{\nabla T}{T} \right] + \rho_g \mathbf{V} \cdot \nabla x_k = \dot{S}_{v,c_k}$	in gas channels and porous electrodes	(4.51a)
$\rho_g (\mathbf{V} \cdot \nabla) \mathbf{V} = \nabla \cdot \left[-p \mathbf{I} + \mu_m (\nabla \mathbf{V} + (\nabla \mathbf{V})^T) - \left(\frac{2}{3} \mu_m - \kappa_{dv} \right) (\nabla \cdot \mathbf{V}) \mathbf{I} \right] + F$	? (in gas channels)	(4.51b)
$-\frac{B}{\mu_m} \nabla p = \mathbf{V}$	in porous electrodes	(4.51c)

CONTINUATION OF TABLE 4.12

$\frac{\sigma_k^{\text{surf}}}{\Gamma} \dot{S}_{v,C_k} = -\nabla \cdot (D_k^{\text{surf}} \nabla \theta_k), \quad \text{where} \quad \theta_k = \frac{C_k \sigma_k^{\text{surf}}}{\Gamma}$			in porous electrodes	(4.51d)
Constitutive Equations and Parameters				
$D_{j,k}^{\text{eff}} = \left(\frac{\tau^2}{\varepsilon D_{j,k}} + \frac{1}{D_k^{\text{Kn,eff}}} \right)^{-1}$			in porous electrodes	(4.51e)
$B = \frac{\varepsilon^2 \bar{d}_{pa}^2}{150(1 - \varepsilon)^2}$			in porous electrodes	(4.51f)
Porous structure thickness (μm):	350			
Porosity ε (%):	40			
Tortuosity factor τ^2 (-):	$[(3 - \varepsilon)/2]^{0.5}$		in anode	
Average particle diameter $\bar{d}_{pa}$ (μm):	2			
Surface site density of Ni Γ (mol cm^{-2}):	6.1×10^{-9}			
Assumptions and Remarks				
<p>i. Equation (4.51a) allegedly represents the mass transport equation for the k-th species. This equation, identified by the authors as “Stefan-Maxwell transport equation”, has indeed several critical problems:</p> <ol style="list-style-type: none"> Seemingly, the first term on the LHS (within the brackets) is probably what made the authors relate it to the Maxwell-Stefan theory; however, such nomenclature is incorrect. Solely by the way in which this term has been written one cannot really assert this relation. It may rather be identified with the so-called “generalized diffusion driving force”, as it became known from the TIP theory^[159, 80, 161], which in the case of Eq. (4.51a) also includes the thermophoretic “force” (Soret effect). Moreover, the term $D_{j,k}^{\text{eff}}$ in this equation is in complete disagreement with that of the standard Maxwell-Stefan model^[185]. The applied definition of diffusive flux has issues related to the frame of reference, <i>e.g.</i>, this definition is not frame indifferent/invariant. The definition of diffusive flux, when taking into account Eq. (4.51e), has problems to enforce mass conservativity because it applies a non-conservative form of fluxes (see note “i-a”). The second term on the LHS is inconsistent with the description of Eq. (4.51b) because in the former it is implicitly assumed that the field of mean-flow velocity is constant. The dimension consistency of the first term on the RHS is questionable, based on the expression given by Eq. (4.51d), <i>i.e.</i>, apparently $\dot{S}_{v,C_k}$ has the dimension of $\text{mol s}^{-1} \text{cm}^{-3}$ whereas Eq. (4.51a) has the dimension of $\text{kg s}^{-1} \text{m}^{-3}$. The authors have informed that this equation is applied in both gas channels and porous domains, which is obviously a misleading statement, <i>e.g.</i>, Eq. (4.51e) is only valid for porous media. <p>ii. These authors referred to Eq. (4.51b) as the “weakly compressible Brinkman equation”. Not really sure why they gave such identification, as the authors have stated that this equation is to be applied in the gas channel (homogeneous fluid domain).</p> <ol style="list-style-type: none"> The last (source?) term on the RHS (“F”) was left unidentified/unspecified in their paper, and so it was the parameter κ_{dv}. The physical significance of the term $(2/3) \mu_m - \kappa_{dv}$ is obscure (note the use of a negative sign). Perhaps it alludes to the coefficient of bulk viscosity¹¹. If so, in this case it is not reasonable to affirm that the thermodynamic pressure is not equal to the mean (mechanical) pressure^[314] for “weakly compressible” flows. 				

¹¹ Not to be confused with the second coefficient of bulk viscosity or dilatational viscosity^[314].

CONTINUATION OF TABLE 4.12

- iii. Equation (4.51d) is the transport equation for surface species (for those participating in electrochemical reactions at the TPB). Distinctively from the previous works presented in this chapter, surface diffusion phenomenon was considered by Xie and Xue (the hypothesis of local equilibrium with adsorption/desorption processes is implied). A Fickian-type description has been used for the surface diffusion term; however, no specification (or value) was attributed to D_k^{surf} .
- iv. No indication was given on how $D_k^{\text{Kn,eff}}$ was calculated. Note that in Eq. (4.51e) the Knudsen diffusion coefficient is not multiplied by ε/τ^2 , only the mutual (“bulk”) diffusion coefficient.

Table 4.13: Macro-homogeneous model from Xie *et al.* (309); Xie and Xue [310]**Governing Equations Coupled to Constitutive Equations (i.e., Transport Equations)**

$$\nabla \cdot \left[-\rho_g x_k \sum_j D_{j,k}^{\text{eff}} \left(\nabla y_j + (y_j - x_j) \frac{\nabla p}{p} \right) \right] + \rho_g \mathbf{V} \cdot \nabla x_k = \dot{S}_{\mathbf{V},x_k} \quad \text{in porous electrode} \quad (4.52a)$$

$$\nabla p + \rho_g (\mathbf{V} \cdot \nabla) \mathbf{V} = \nabla \cdot \left[\mu_m (\nabla \mathbf{V} + (\nabla \mathbf{V})^\top) - \frac{2}{3} \mu_m (\nabla \cdot \mathbf{V}) \mathbf{I} \right] \quad \text{in gas channel} \quad (4.52b)$$

$$\nabla \cdot (\rho_g \mathbf{V}) = 0 \quad \text{in gas channel} \quad (4.52c)$$

$$\frac{B}{\mu_m} \mathbf{V} = -\nabla p + \frac{1}{\varepsilon} \nabla \cdot \left[\mu_m (\nabla \mathbf{V} + (\nabla \mathbf{V})^\top) - \frac{2}{3} \mu_m (\nabla \cdot \mathbf{V}) \mathbf{I} \right] \quad \text{in porous electrode} \quad (4.52d)$$

Constitutive Equations and Parameters

$$D_k^{\text{Kn}} = \bar{r}_p \frac{2}{3} \left(\frac{8 \mathcal{R} T}{\pi M_k} \right)^{1/2} \quad (\text{to be used with Eq. [4.51e]}) \quad \text{in porous electrode} \quad (4.52e)$$

Assumptions and Remarks

- i. In relation to the mass transport Eq. (4.52a), the thermodiffusion term is now absent and the notation for the source term ($\dot{S}_{\mathbf{V},x_k}$) was corrected, so to reflect a mass-based rate ($\text{kg s}^{-1} \text{m}^{-3}$).
- ii. The momentum equation, Eq. (4.52b), for the gas channel was also changed. Now it is recognized as the steady-state “compressible” Navier-Stokes equation for the mean flow. The continuity equation, Eq. (4.52a), was made explicit as well (observing that no sources terms were included in this equation).
- iii. The momentum equation, Eq. (4.52d), for porous electrodes was also changed. In their prior work, Darcy’s Law was used to describe the macroscopic flow in the porous domain; here a Brinkman-type equation is adopted. There is an additional “detail” in this equation: the presence of a porosity factor ($1/\varepsilon$) in front of the second term of RHS. Although it is not possible to say that this form is “incorrect” (because explicit definitions for both B and μ_m would be required^[301, 303]), it certainly produces ambiguity between the LHS and RHS of Eq. (4.52d) with respect to whether $\mathbf{V}$ is a superficial velocity or not.

Table 4.14: Macro-homogeneous model from Jin and Xue [312].

Governing Equations Coupled to Constitutive Equations (i.e., Transport Equations)

$$\nabla \cdot \left\{ \rho_g x_k \mathbf{V} - \rho_g x_k \sum_j D_{j,k} \left[\frac{\bar{M}_n}{\bar{M}_j} \left(\nabla x_j + x_j \frac{\nabla \bar{M}_n}{\bar{M}_n} \right) + (y_j - x_j) \frac{\nabla p}{p} \right] \right\} = \dot{S}_{\mathbf{V},x_k} \quad \text{in gas channels} \quad (4.53a)$$

CONTINUATION OF TABLE 4.14			
$\nabla \cdot \left\{ \rho_g x_k \mathbf{V} - \rho_g x_k \sum_j D_{j,k}^{\text{eff}} \left[\frac{\bar{M}_n}{M_j} \left(\nabla x_j + x_j \frac{\nabla \bar{M}_n}{\bar{M}_n} \right) + (y_j - x_j) \frac{\nabla p}{p} \right] \right\} = \dot{S}_{v,x_k}$	in porous electrodes	(4.53b)	
$\rho_g (\mathbf{V} \cdot \nabla) \mathbf{V} = \nabla \cdot \left[-p \mathbf{I} + \mu_m \left(\nabla \mathbf{V} + (\nabla \mathbf{V})^\top - \frac{2}{3} (\nabla \cdot \mathbf{V}) \mathbf{I} \right) \right]$	in gas channels	(4.53c)	
$\nabla \cdot (\rho_g \mathbf{V}) = 0$	in gas channels	(4.53d)	
$\left(\frac{\mu_m}{B} + \dot{S}_{v,m} \right) \mathbf{V} = \nabla \cdot \left[-p \mathbf{I} + \frac{\mu_m}{\varepsilon} \left(\nabla \mathbf{V} + (\nabla \mathbf{V})^\top - \frac{2}{3} (\nabla \cdot \mathbf{V}) \mathbf{I} \right) \right]$	in porous electrodes	(4.53e)	
$\nabla \cdot (\rho_g \mathbf{V}) = \dot{S}_{v,m}$	in porous electrodes	(4.53f)	
Constitutive Equations and Parameters			
$D_{j,k}^{\text{eff}} = \frac{\varepsilon}{\tau^2} \left(\frac{1}{D_{j,k}} + \frac{1}{D_k^{Kn}} \right)^{-1}$	in porous electrodes	(4.53g)	
$D_k^{Kn} = \frac{97}{2} \bar{d}_p \left(\frac{T}{M_k} \right)^{1/2}$	in porous electrodes	(4.53h)	
Source Terms			
$\dot{S}_{v,m} = \sum_{i=1}^{N_{\text{reac}}} \frac{i_F M_i}{z_{e,i} \mathcal{F}}$	(where N_{reac} represents the number of electrochemical reactions)	in porous electrodes	(4.53i)
Assumptions and Remarks			
<p>i. The mass transport Eq. (4.53b) is equivalent to Eq. (4.52a), with the difference being that the former is expressed in terms of mass fractions and the latter in terms of mole fractions. Thus, the additional terms appearing in Eq. (4.53b) are due to the transformation Jacobian^[315, 316] to change from ∇y_j to ∇x_j.</p> <p>ii. It is worth noting that in the momentum Eq. (4.53e), differently from all other works presented so far, an “total” mass source term ($\dot{S}_{v,m}$) appears, which is a direct result from the form of the continuity Eq. (4.53f). However, similarly to what was said in Table 4.13 (note “iii”), $\dot{S}_{v,m}$ should have been divided by ε^2 in Eq. (4.53e). Other authors^[317, 318] have proposed similar equations considering this mass source term.</p> <p>iii. Equation (4.53h) is equivalent to Eq. (4.52e). The seemingly different format is because in Eq. (4.53h) the average pore diameter $\bar{d}_p$ is given in cm and hence D_k^{Kn} is expressed in $\text{cm}^2 \text{s}^{-1}$.</p> <p>iv. In Eq. (4.53i) $\dot{S}_{v,m}$ is the mass source term induced by electrochemical reactions, which is related to the Faradaic charge transfer current density (i_F). In this equation, $z_{e,i}$ represents the moles of electrons transferred per mole electroactive reactant in the i-th reaction (<i>i.e.</i>, $z_{e,i} = z_e/v_i$); and M_i is the molar mass of the electroactive reactant in the i-th reaction.</p>			

Table 4.15: Macro-homogeneous model from Jin and Xue [313].

Governing Equations Coupled to Constitutive Equations (<i>i.e.</i> , Transport Equations)			
$\nabla \cdot \left\{ \rho_g x_k \sum_j D_{k,j}^{\text{eff}} \left[\frac{\bar{M}_n}{M_j} \left(\nabla x_j + x_j \frac{\nabla \bar{M}_n}{\bar{M}_n} \right) \right] \right\} = \dot{S}_{v,x_k}$	in porous electrodes	(4.54a)	

CONTINUATION OF TABLE 4.15		
Constitutive Equations and Parameters		
$D_{k,j}^{\text{eff}} = \frac{\varepsilon}{2\tau^2} \left[\left(\frac{1}{D_{k,j}} + \frac{1}{D_k^{Kn}} \right)^{-1} + \left(\frac{1}{D_{k,j}} + \frac{1}{D_j^{Kn}} \right)^{-1} \right]$	in porous electrodes	(4.54b)
Assumptions and Remarks		
<p>i. The mass transport Eq. (4.54a) now disregards both the “advective” flux¹² and also the pressure gradient as an additional diffusion driving “force”. Thus, here one has a pure reaction-diffusion equation (RDE).</p> <p>ii. The authors have proposed Eq. (4.54b) as an <i>ad hoc</i> method to avoid the violation of gas species mass conservation (which, in fact, happens if ∇p is taken as zero, as indicated in APPENDIX A). An “average” Bosanquet diffusion coefficient is employed^[72].</p>		

4.5.2.7 Dong *et al.*

As a final example of possible variation of the momentum equation in porous electrodes (*i.e.*, specifically to macro-homogeneous models from the SOFC literature) is the inclusion of extra source terms that account for other frictional effects, *e.g.*, Forchheimer term. Dong *et al.*^[319] have considered such modification for the numerical (CFD) analysis of a planar anode-supported SOFC stack (see Table 4.16 for the model equations).

Table 4.16: Macro-homogeneous model from Dong <i>et al.</i> [319]		
Governing Equations Coupled to Constitutive Equations (<i>i.e.</i>, Transport Equations)		
$\nabla \cdot (\rho_g \mathbf{V} \mathbf{V}) = -\nabla p + \nabla \cdot \bar{\bar{\tau}}_v + \dot{S}_{v,v} \quad \text{with} \quad \bar{\bar{\tau}}_v = \mu_m \left(\nabla \mathbf{V} + (\nabla \mathbf{V})^T - \frac{2}{3} (\nabla \cdot \mathbf{V}) \mathbf{I} \right)$	in porous electrodes	(4.55a)
Source Terms		
$\dot{S}_{v,v} = - \left(\frac{\mu_m}{B} \mathbf{V} + \frac{1}{2} \rho_g C_{fo} \mathbf{V} \mathbf{V} \right)$	in porous electrodes	(4.55b)
Assumptions and Remarks		
<p>i. In Eq. (4.55b) the second term on the RHS is the so-called Forchheimer “correction”; the friction or inertial resistance factor C_{fo} is known as Forchheimer factor.</p>		

¹² Briefly, in this dissertation the term “advection” is understood as the transport mechanism of a conserved property (or simply of a scalar) by a fluid due to fluid's bulk motion in relation to its virtual center of mass. In the literature (mainly in the CFD area), the convective flux of single fluids is usually defined as being equivalent to advection. Here, however, the former will be defined as the total flux of a conserved property (“diffusion plus advection”) in superimposed fluids. Surely, such convention is not without controversies and it is far from being considered as a generally agreed convention.

4.5.2.8 Special Topics on the Modeling of Porous SOFC Layers

There are still a large number of works in the literature devoted to, or that incorporated to some extent, the evaluation of concentrations polarization in SOFCs using the macro-homogeneous approach. Nonetheless, they abide by the same mathematical models as the ones reviewed in this section. Thus, to not overwhelm this monograph with endless listings of similar models, these other works will not be appraised herein. In Table 4.17, nonetheless, some of these works are indicated as representative of the models that have been heretofore discussed.

Table 4.17: Other meaningful works applying/reviewing macro-homogeneous models of porous SOFC layers.		
Based on DGM, <i>e.g.</i> as per Tables 4.6 and 4.8	Based on MFM, <i>e.g.</i> as per Tables 4.9 and 4.13	Comparison/Review of Different Mass Transfer Models
García-Camprubí <i>et al.</i> [320, 321] Bertei <i>et al.</i> [85] Hu <i>et al.</i> [322]	Li <i>et al.</i> [323] Lee <i>et al.</i> [324] Nerat and Juričić [325] Ramírez-Minguela <i>et al.</i> [326]	Vural <i>et al.</i> [327] Nishi <i>et al.</i> [328] Wang <i>et al.</i> [273] Xu <i>et al.</i> [329] Yuan and Sundén [330] Bao <i>et al.</i> [331]

A number of more specific topics related (directly or indirectly) to concentration-induced voltage losses in SOFCs have not been included (in detail) in this review, even though there are macro-homogeneous models in the literature that deal with these topics, as for instance:

- i. Surface-mediated diffusion (and other first-passage phenomena).
- ii. The influence of gas-phase equilibrium potential on electrode kinetics (for which some discussion was already given in §§2.3 and §§3.3).
- iii. Material constitutive models of composite electrodes, which are pertinent to evaluate transport properties and other relevant parameters.
- iv. The effect of the variability of modeling parameters on simulation results.

Evidently, given that the topics listed above constitute, by themselves, a special thematic, the respective literature will not be scrutinized in in this dissertation.

4.5.3 Some Concluding Remarks on Macro-Homogeneous Models

So far, it has not been the intent of this chapter to go into the specifics of each model (and this remains true for the rest of this section). Nevertheless, a number of remarks may be drawn at this point based on those considerations provided at the end of §§4.5.1. Most of the numerical simulations of SOFC in the literature, which apply the macro-homogeneous approach, do not perform any pre-assessment regarding the validity, physical pertinence, and potential limitations of their mathematical models. It appears that an “intellectual inertia” exist to a great extent. Not in the sense that the existing modeling approaches really represent a de

facto state of art (for which neither improvement nor corrections would be necessary), but rather, unfortunately, some thoughtless “establishment”. The same set of modeling equations (some of them with fragrant errors, as indicated in the foregoing pages) have been reused in different works (at times by the same authors) to simulate both the “simplest” case and the more complex multiphysics case, without any modification whatsoever; and there always seems to be fair agreement with empirical observation. The ubiquitous argument to persist with these approaches is therefore their seeming validation against experimental results. In some cases, however, their apparent success is certainly illusory. Thus illusory conclusions may be drawn from these “validated” results, engendering confusion and controversial perceptions.

Considering the models reviewed in §§4.5.2, one verifies that they try to represent the “average features” of the random and complicated microscopic geometry of the porous electrode using mainly two concentrated parameters, namely porosity (ε) and tortuosity (τ). These parameters are, more often than not, empirically adjusted values to fit experimental data. That is, they are really employed as “fudge factors”. In this situation, however, one cannot objectively assess if the combination of these two factors does, in fact, represent a reasonably accurate average of the “microscopic features” on the macroscale. It can also be seen that, in the case of modeling equations that were presented, explicit factors accounting for correction of specific interfacial areas are seldom available, especially at phase boundaries or to differentiate the usage of transport equations in distinct physical domains (e.g., active layer and support substrate). Usually these factors, when available, are restricted to the description of electrochemical reactions “inside” rate expressions (*i.e.*, in source terms only). Thus, the correction of species fluxes and superficial current densities do not occur in a transparent manner. In this case, the “area conversion” of a flux leaving one geometric domain to other neighboring domain is therefore not handled properly.

None of the works reviewed so far has provided any comments on the ratio of the characteristic length of the microstructure to the length characteristic of the macrostructure size of porous layer. This kind of evaluation is especially critical for thin film SOFC designs (e.g., μ -SOFCs). Furthermore, all the models in §§4.5.2, with the exception of CPIM (Table 4.11), seems to apply an unmindful definition of mass fluxes, which (apparently) are tacitly assumed to be valid averages over the pore geometrical cross-section. In other words, these macro-homogeneous models, besides ignoring any analysis of possible significant effects due to the variation of gas properties across the pore diameter, they are also unclear when defining if the flux is based on an apparent, averaged superficial velocity or calculated based on the actual velocity within the open pore volume. The importance of such coherence is not only semantic, but it can also impact, for instance, the definition of porous media constitutive

equations and parameters. One can say at least that there is certain sloppiness in the notation used by these models. Finally, about the last consideration in §§4.5.1, the issue it is not the fact the characteristic time for gas diffusion is not compared to that for electrically charging the double-layer capacity (which is usually of minor practical significance within the context of fluid flow and mass transfer in the gas-phase), but instead the absence of discussion about the many other (possible) timescales of competing physicochemical processes or relaxation phenomena, which might adversely hinder the validity of a chosen mathematical model (see §§3.6).

4.6 Single-Scale Models III: Multiphysics in Mesoscale (and Beyond)

Certainly, single-scales models are not limited to describe the macroscale. They can be implemented on a great range of spatial–temporal scales, encompassing many braches of physical-chemistry and molecular physics. In theory, single-scale models can be developed on the smallest physical scale one can possibly think of, but their validity are subjected to the limitations of a local minimum scale on which the usage of the respective “governing” equations is still valid. A prominent example of such wide-ranging spectrum of implementations is the molecular reaction dynamics^[332], which aims to provide a description of reaction chemistry on the fundamental scale of individual atoms and molecules.

On what concerns solid-oxide fuel cells, specifically, existing modeling methodologies range from the atomistic to the system scale^[1, 2] by virtue of the fact that SOFCs are intrinsic multiscale systems. The reason is the necessity of focusing on an individual scale in order to make possible the study of complete systems (see §§1.4). Sub-macroscale modeling methodologies constitute a broad category of examples in the SOFC literature. In this dissertation, however, one is only interested in those works that have meaningful nexus to concentration polarization (*i.e.*, transport phenomena within the gas-phase). This severely restricts the number of published works under examination, as the vast majority of them devote their analysis either to the understanding of surface reactions taking place at the phase boundaries of electrodes/electrolytes, or to solid-phase transport phenomena (*e.g.*, membrane-polarization processes related to charge transport). Among the works that have pertinence to mass transport limitations and concentration-induced voltage losses, a significant part is dedicated to the mesoscale microstructural analysis and characterization of porous electrodes. The pertinence is justified by the fact that these works are able to provide relevant information on the microstructure of porous medium with high (sub-micrometer) spatial resolution, which

can be “homogenized” (e.g., through correlations or “embedded” microscale simulations) and subsequently used by macroscale-continuum (macro-homogeneous) modeling approaches; or, alternatively, they can be directly represented in the model through the so-called structure-resolved approaches. The latter case is what will be effectively discussed in this section. The former case will be addressed in §§4.7 and §§4.8.

4.6.1 Geometrical Modeling and Reconstruction of Porous Electrodes

Structure-resolved models may be “partially resolved” or “fully resolved”. Fully resolved models use information obtained from tridimensional¹³ (3D) reconstruction of real (or virtual) samples of electrodes (or porous supports), which enable one to directly probe the effects of electrode geometry on transport phenomena. Partially resolved models apply some family of theoretical methods based on idealized material models (e.g., percolation theory), which use a number of empirical physical characteristics as input. Partially resolved models are usually developed in the form of algebraic correlation formulas, making their application comparatively simpler. For this reason, there are works in literature that have applied fully resolved simulations to derive partially resolved models^[333, 334].

The 3D reconstruction of real samples (see Table 4.18 for references) apply reconstruction techniques based on high-resolution imaging technologies, such as focused ion beam scanning electron microscopy (FIB-SEM) or X-ray computed tomography (XCT). The 3D microstructure of electrode is virtually reconstructed in a computational field: in the FIB-SEM (destructive) technique, this reconstruction is done using a series of acquired 2D SEM images (each sequential image is obtained by gradually milling down through the electrode thickness); whereas in the XCT (nondestructive) technique the retrieved information is “naturally” in the form of 3D objects (“virtual slices” that represent cross-sections of electrode and that can be used directly to create a 3D virtual model). Virtualized microstructures are then quantified by means of mathematical analyses, which can estimate the properties of interest, such as TPB density, tortuosity, porosity, and volume fractions of existing phases.

¹³ Two-dimensional selected regions (“thin cross-sections”) of electrodes have also been used as input information in numerical (2D) simulations; or to reconstruct the 3D geometry of an electrode (e.g., as in stochastic reconstruction).

Table 4.18: References on the reconstruction of porous electrodes

Reference	SOFC Component		Sample Reconstructed		Experimental Technique			Scope of the Modeling			Modeling Method	
	Anode	Cathode	Real	Virtual	FIB/SEM	XCT	Other	Material Properties	Transport Phenomena	Chemical Reactions	LBM	Other
Suzue <i>et al.</i> [335] ^{▲▲♦}	•		•				•	•	•	•	•	
Kenney <i>et al.</i> [17] [▲]		•		•				•				•
Wilson <i>et al.</i> [336]	•		•		•			•				•
Iwai <i>et al.</i> [337] ^{▲♦}	•		•		•			•			•	•
Joshi <i>et al.</i> [338] ^{▲♦}	•		•	•		•		•	•		•	•
Shikazono <i>et al.</i> [91] ^{▲♦}	•		•		•			•	•	•	•	
Grew <i>et al.</i> [339] [▲]	•		•			•		•				•
Grew <i>et al.</i> [340] [▲]	•		•			•		•	•		•	
Vivet <i>et al.</i> [341] [▲]	•		•		•			•	•			•
Kanno <i>et al.</i> [102] ^{▲♦}	•		•		•			•	•	•	•	
Kishimoto <i>et al.</i> [342] ^{▲♦}	•		•		•			•	•	•		•
Berson <i>et al.</i> [343] [▲]				•				•	•			•
Cai <i>et al.</i> [333] [♦]	•			•				•	•	•		•
Matsuzaki <i>et al.</i> [145] ^{▲♦}		•	•		•			•	•	•	•	
Holzer <i>et al.</i> [123] [▲]	•		•		•			•				•
Laurencin <i>et al.</i> [344] ^{▲♦}	•		•			•		•	•			•
Joos <i>et al.</i> [345] ^{▲♦}		•	•		•			•	•			•
Paradis and Sundén [346] ^{▲*}	•		•				•		•	•	•	
Bertei <i>et al.</i> [334] ^{▲♦}	•	•		•				•	•	•		•
Cronin <i>et al.</i> [347] [▲]	•	•	•			•		•				•
Holzer <i>et al.</i> [348] [▲]	•		•		•			•				•
Chen-Wiegart <i>et al.</i> [349] [▲]		•	•			•		•				•
Joos <i>et al.</i> [350] [▲]	•		•		•			•				•
Guan <i>et al.</i> [351] [▲]	•		•			•		•	•	•	•	
Espinoza <i>et al.</i> [352] ^{▲*}		•	•				•		•	•	•	
Kong <i>et al.</i> [353] ^{▲♦}	•	•		•				•	•			•
Lichtner <i>et al.</i> [354] [▲]		•	•		•			•				•
Pecho <i>et al.</i> [355] [▲]	•		•		•			•				•
Reiss <i>et al.</i> [356] ^{▲♦}						•		•	•			•
Neumann <i>et al.</i> [357] [▲]	•	•		•				•				•

Notes:

▲: Relevant reference in this dissertation.

▲♦: 3D stochastic reconstruction technique from 2D cross-section images.

♦: Solved transport phenomena equations using methods for which the hypothesis of continuum is implied, at least in part.

*: Two-dimensional simulation based on 2D cross-section images.

In order to compute effective material properties (e.g., gas effective diffusion within the porous matrix) the reconstructed 3D data can be used in numerical simulations as phase boundary information. For instance, Lattice-Boltzmann Methods (LBM) have been applied for this task (see Table 4.18 for references). There are also micro-modeling methods that use material models with minimal or no experimental data as input^[334, 17, 338]. The advantage of the latter methods is that effective transport properties can be evaluated without resorting to empirical correlations or parameters fitted to experimental data. For example, these properties can be estimated using Monte Carlo random walk methods running on virtual electrodes, which were numerically constructed through sphere packing algorithms^[358].

An expressive part of the works in Table 4.18 seeks only the obtainment of microstructure information of SOFC layers on the mesoscale level. This information is then usually used in either of two ways. In the first, it can provide lumped or homogenized microstructure parameters (e.g., porosity, tortuosity, constriction, and percolation factors) for the calculation of effective transport properties (e.g., effective diffusion coefficient), which then can be used in macroscale-continuum models (such as in **§§4.5.2**). In the second way, it provides detailed geometrical information of the physical domain (pore-phase or fluid domain; solid-phase or “walls”) over which gas transport equations can be directly solved. In order to solve these equations on the mesoscale level, LBM is often applied, although other methods such as FVM and FEM have also been employed for this purpose (see **§§4.6.2.6**). It is important to emphasize that the mere fact of solving transport equations on the “geometrical mesoscale” does not mean that the problem's physics is evaluated in its entirety on the mesoscale level. This is because, besides the detailed geometric information, the form of governing and constitutive equations also dictates the description level of the problem. This point will be briefly seen in **§§4.8**.

As mentioned earlier, partially resolved models use theoretically idealized material models that rely, to some extent, on empirical input data. Certainly, the goal of these simpler micro-geometry modeling methods is to use the minimum possible amount of experimental data as input, akin to methods that “reconstruct” 3D virtual samples of porous electrodes. The output of these partially resolved models finds its best application in macro-homogeneous models, as the former is able to provide the necessary lumped microstructure parameters used by the latter (see **§§4.7**). The more commonly used geometrical models have been developed to predict the influences of microstructural properties on certain “higher level properties”, which can then be applied in macroscale-continuum models. For example, they can predict the influence of solid grain size, pore size, and porosity on the TPB length (λ_{tpb}) of composite electrodes^[359, 360]. Among partially resolved models there is the family of methods built upon

the statistical-based percolation theory^[361], which include models^[362, 363] that accounts for the presence of polydispersed powders and pore formers in composite electrodes, predicting effective properties such as the surface area and the mean hydraulic radius of pore phase. Some other percolation models^[364, 365], with considerable generality in their practical application, can also predict ionic and electronic effective conductivities. Table 4.19 provides a list of reference works that dealt with constitutive, partially resolved models of SOFC electrodes.

Table 4.19: References on partially resolved models (“geometrical models”) of porous electrodes.

Reference	SOFC Electrode		Electrode Properties (IP: Input Parameter; OP: Output Property)													
	Anode	Cathode	Solid Grain Size (of each phase)	Pore size	Porosity	Volume Fraction (of each phase)	Coordination Number	Particle Contact Angle	Fractional Overlap Between Particles	Distance Between Particles	Phase Contact Area	Specific Surface Area	Volume Specific TPB Length	Area Specific TPB Length	Effective Conductivity	Mean Pore Hydraulic Radius
Deng and Petric [359]	•	•	IP	IP	IP								OP			
Nam and Jeon [366]♦	•	•	IP		IP	IP	IP	OP		IP			OP	OP		
Janardhanan <i>et al.</i> [360]	•	•	IP			IP	IP		IP				OP			
Chen <i>et al.</i> [364]♦	•	•	IP		IP	IP	IP	IP			OP		OP	OP	OP	OP
Bertei and Nicolella [362]♦	•	•	IP		IP	IP	IP	IP			OP	OP	OP			OP
Chen <i>et al.</i> [363]♦	•	•	IP		IP	IP	IP	IP						OP	OP	OP
Bertei <i>et al.</i> [367]♦		•	IP		IP	IP	IP	IP					OP		OP	OP
Chen <i>et al.</i> [365]♦	•	•	IP		IP	IP	IP	IP			OP		OP	OP	OP	OP
Notes: ♦ : Based on percolation theory.																

Formally, neither the porosity nor tortuosity is evaluated as an output property using the models from Table 4.19. However, as a “backward problem”, the porosity, for instance, might be calculated using these models if an output property (e.g., TPB length) is given as known.

4.6.2 Structure-Resolved Models of Gas Transport in Porous SOFC Layers

As highlighted in **Chapter 1**, the microstructure features of porous electrodes play a major influence on the performance of SOFCs and thus microstructural design constitutes a key part in the research and technology development of materials. Assuming that the basic engineering of new materials can be successfully accomplished by evaluating the effects of certain idealized microstructural parameters, modeling techniques that directly use these parameters (to predict cell performance) are therefore evidently relevant in streamlining the technology development process. General criteria to support the selection of different modeling techniques were discussed in §§1.4. Based on that discussion, structure or microstructure resolved models are computationally expensive techniques and hence their application is usually only feasible to small, representative volume elements (RVE) of the porous electrode (typically in the range of $1 \times 10^3 \mu\text{m}^3$ to $5 \times 10^3 \mu\text{m}^3$ for 3D samples¹⁴). In other words, numerical simulation is limited to (comparatively) quite small samples of the electrode material under study. On the other hand, macroscale-continuum models are far less computationally intensive and thus they allow easier larger-scale description of a complete single-cell body.

However, in addition to the trade-offs related to time-consuming calculations, one must question how physical scale information can affect the accurate description of transport phenomena that is controlled by certain physical characteristic scales. For instance, to what extent the system of interest is, in fact, governed by macroscopic mass, momentum, and heat transfer; and to what extent “subgrid-scale” phenomena need to be properly resolved and hence cannot be undervalued. That is, to what degree one needs to include small scale information as a subset of the contents of larger scale physical-chemical processes, in order to represent important small scale physical-chemical processes that occur on spatio-temporal scales that cannot, otherwise, be adequately resolved on a macroscopic computational mesh. Structure-resolved models of porous components aim to increase the confidence level in explaining the macroscopic performance of SOFCs. These models, “by revealing what takes place in the underground”, are geared to give better “control” of material design parameters. Representative examples of such models, which directly incorporate microstructural information on the mesoscale, are presented in what follows (see full listing in Table 4.18). Nevertheless, “advanced topics” on porous media characterization (including measurement techniques, calculation methods, and analysis of microstructural properties) will not be appreciated in this work.

¹⁴The determination of RVE is a critical step in microstructure resolved simulations of porous layers, especially when the sample volume size can affect numerical results. See Joss *et al.*^[345] and other references in Table 4.18.

4.6.2.1 Suzue, Iwai, Shikazono, Kanno, Matsuzaki, and Coauthors

Researchers from The University of Tokyo developed a series of studies^[335, 337, 91, 102, 145] in which the FIB/SEM technique¹⁵ was combined with LBM to evaluate the performance of electrode microstructures. In these studies, it is noteworthy the development and discussion of new numerical methods to quantify the microstructure properties of 3D reconstructed computational domains, such as TPB length, volume fractions, connectivities, and tortuosities of the involved phases (e.g., pore, ionic, and electronic phases). In one of their papers^[337], random walk calculations were also used for comparison with LBM in evaluating tortuosity factors. The authors have not consistently applied the same mathematical models throughout their works and significant differences exist. Tables 4.20 and 4.21 include information for comparing them.

For the sake of clarity, it should first be noted that the diffusion problem is actually solved by means of LBM; the continuum transport equations shown in the following tables (and also by the authors in their original papers) are mainly used as mathematical archetypes (*i.e.*, “idealized statements”) for the phenomena they seek to represent. The reason for that is the general form of LBM equations, which encapsulates the physics of the problem under consideration and thus, in this case, “the conventional” transport equations of continuum physics convey (more clearly) the idea that “a diffusion model” is being addressed. Nonetheless, these “archetypes equations” play a key function in defining how the diffusion coefficient should be evaluated in the LBM model itself in order to calculate the necessary (single) relaxation time.

Table 4.20: Structure resolved model from Suzue *et al.* [335]

Combination of Governing and Constitutive “Laws” for Continua (<i>i.e.</i> , Archetype Continuum Transport Equations)			
$\nabla \cdot (D \nabla C_{H_2}) = \dot{S}_{V, C_{H_2}}$	see “Numerical Scheme” and “Assumptions and Remarks” below for explanations on how this equation was actually solved.	in porous electrodes	(4.56a)
$\nabla \cdot (\sigma_e \nabla \phi_{an}) = \dot{S}_{V, \phi_{an}}$	see “Numerical Scheme” and “Assumptions and Remarks” below for explanations on how this equation was actually solved.	in porous electrodes	(4.56b)
$\nabla \cdot (\sigma_{io} \nabla \phi_{elyt}) = \dot{S}_{V, \phi_{elyt}}$	see “Numerical Scheme” and “Assumptions and Remarks” below for explanations on how this equation was actually solved.	in porous electrodes	(4.56c)
Constitutive Equations and Parameters			
$D = y_{H_2} D_{H_2} + y_{H_2O} D_{H_2O}$		in porous electrodes	(4.56d)

¹⁵In Suzue *et al.*^[335] the authors applied a stochastic reconstruction technique in place of FIB/SEM. This reconstruction technique is based on the scheme originally proposed by Yeong and Torquato^[421], which statistically reconstructs 3D porous media from selected 2D cuts (SEM images) of the sample.

CONTINUATION OF TABLE 4.20

$$D_{H_2} = \left(\frac{1}{D_{H_2, H_2O}} + \frac{1}{D_{H_2}^{Kn}} \right)^{-1} \quad \text{in porous electrodes} \quad (4.56e)$$

$$D_{H_2O} = \left(\frac{1}{D_{H_2, H_2O}} + \frac{1}{D_{H_2O}^{Kn}} \right)^{-1} \quad \text{in porous electrodes} \quad (4.56f)$$

The binary gas diffusion coefficient D_{H_2, H_2O} is calculated using a standard Chapman–Enskog theory^[263].

$$D_k^{Kn} = \bar{r}_p \frac{2}{3} \left(\frac{8RT}{\pi M_k} \right)^{1/2}, \quad \text{for } k = H_2, H_2O \quad \text{in porous electrodes} \quad (4.56g)$$

Source Terms

$$\dot{S}_{V, C_{H_2}} = \begin{cases} -\frac{i_0 \lambda_{tpb}}{2F} \left[\exp\left(\frac{2F}{RT}\eta\right) - \exp\left(-\frac{F}{RT}\eta\right) \right] & , \text{ at the TPB} \\ 0 & , \text{ elsewhere} \end{cases} \quad (4.56h)$$

$$\dot{S}_{V, \phi_{an}} = 2F \dot{S}_{V, C_{H_2}} \quad \text{in porous electrodes} \quad (4.56i)$$

$$\dot{S}_{V, \phi_{elyt}} = -2F \dot{S}_{V, C_{H_2}} \quad \text{in porous electrodes} \quad (4.56j)$$

$$\eta = \phi_{an} - \phi_{elyt} \quad \text{in porous electrodes} \quad (4.56k)$$

$$i_0 = 31.4 \times p_{H_2}^{-0.03} p_{H_2O}^{0.40} \exp\left(-\frac{1.83 \times 10^4}{T}\right) \quad \text{in porous electrodes} \quad (4.56l)$$

Lattice-Boltzmann Method (“Numerical Scheme”)

The LBM was used by Suzue *et al.*^[335] to solve Eq. (4.56a)-(4.56c) in each respective phase (see “Assumptions and Remarks” below). The Lattice-Boltzmann Equation (LBE) with LBGK operator^[368] was given as :

$$f_i(\mathbf{x} + \mathbf{c}_i \Delta t, t + \Delta t) = f_i(\mathbf{x}, t) - \frac{1}{\tau_c} [f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t)] + \dot{s}_\phi(i, j, k) \Delta t \quad \text{computational domain} \quad (4.56m)$$

Phase-distinguished 2D image (“cut”) of a composite anode sample used in the stochastic reconstruction (Ni: white, YSZ: gray, pore: black).

3D reconstructed microstructure of the anode (Ni: green, YSZ: blue, transparent gray: pore).

Schematics of reaction production at TPB.

Where $\dot{s}_\phi(i, j, k)$ is expressed at the voxel center i, j, k in a discretized form. This source term (i.e., the volumetric current density) at TPB $(i + 1/2, j + 1/2, k)$ was calculated

CONTINUATION OF TABLE 4.20

$$\dot{s}_\phi \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) = -\frac{i_0}{2\mathcal{F}} \lambda_{tpb} \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) \frac{\exp[(2\mathcal{F}/RT)\eta] - \exp[-(\mathcal{F}/RT)\eta]}{\Delta x^3} \quad \text{computational domain} \quad (4.56n)$$

$$\eta = \phi_{an}(i, j, k) - \phi_{elyt}(i+1, j, k) \quad \text{computational domain} \quad (4.56o)$$

Assumptions and Remarks

- i. In the derivation of Eq. (4.56d) it was assumed a binary gas composition of H_2/H_2O and equimolar diffusion (thus constant total pressure, *i.e.*, $p = p_{H_2} + p_{H_2O} = \text{const}$). Therefore, only the diffusion equation of hydrogen is solved, Eq. (4.56a).
- ii. Knudsen “diffusion” was accounted for using the Bosanquet formula, Eq. (4.56e) and (4.56f), wherein the Knudsen diffusion coefficient (Eq. 4.56g) is evaluated assuming a constant mean pore radius (0.75 μm) in all simulated cases.
- iii. One can note the absence of porous medium structural parameters (*e.g.*, porosity, tortuosity, and so on) in the modeling equations, especially in terms of effective transport coefficients, Eq. (4.56a)-(4.56c). This is explained by the fact that these equations are being solved directly on the pore scale, thus the use of effective values is meaningless. The fields of state variables are resolved within the mesoscale and their (averaged) values on the macroscale already incorporate effects due to the microstructure.
- iv. In Eq. (4.56m) f_i represents the velocity distribution function of “fictitious” particles of gas, electron, or ion with velocity¹⁶ c_i in the i -th (link) direction; f_i^{eq} is a Maxwellian local equilibrium distribution (local equilibrium value for the population of particles in the direction of the i -th link); τ_c is the relaxation time; $\mathbf{x}$ represents the stencil point vector (“lattice points”) among voxels; Δt and Δx are the discretized time and space (voxel edge) steps, respectively. For 3D LBM simulations, D3Q15 ($i = 1, 2, \dots, 15$) or D3Q19 ($i = 1, 2, \dots, 19$) models have been commonly used^[369]. In their work, however, Suzue *et al.*^[335] applied the D3Q6 ($i = 1, 2, \dots, 6$) model in the case of SOFCs, affirming that for simple diffusion simulations this model can be used with a slight loss of accuracy.
- v. Point-wise accurate LBM transport equations (4.56m) for charge and species conservation, Eq. (4.56a)-(4.56c), are solved directly on the reconstructed porous layer (3D computational domain represented by cubic voxels). The second and third terms on the RHS of Eq. (4.56m) represent the rate of change in f_i due to binary molecular collisions and thus they approximate the collision operator of Boltzmann equation.
- vi. Oddly enough the authors used a constant relaxation time ($\tau_c = 0.99$), fixed for all simulations (see note “v” in Table 4.21). No further information is given on how this particular time was obtained. Furthermore, f_i^{eq} was also left unspecified (although it is said to be a “Maxwellia distribution”). These issues are of major importance because the collision operator is responsible for the evaluation of the diffusion phenomenon. Thus no clear link has been made with diffusion coefficients from transport equations, *e.g.* Eq. (4.56d), and, as a result of this, the modeling of diffusive processes “became a black box”. Thus, the notes “i” and “ii” provided above are therefore without objective purpose, as one cannot really understand how the information on diffusion was actually handled.
- vii. The production term $\dot{s}_\phi$ on the RHS of Eq. (4.56m) is calculated from the sources terms of Eq. (4.56a)-(4.56c), using a scheme akin to that of Mukherjee and Wang^[370]. A schematic exemplifying the reaction calculation procedure is shown in the figure above.

¹⁶ c_i in Eq. (4.56m) may also be interpreted as a discrete direction or plainly as a numerical quadrature point (representing a direction link) in the LBM. The term c_i is more generally represented using the notation e_i^k , which is the velocity of the k -th chemical species along the i -th discrete direction. In Suzue *et al.*^[335] LBM equations were solved just for one species (H_2) and the extra index is therefore unnecessary.

CONTINUATION OF TABLE 4.20

- viii. There is a notation error in Eq. (4.56l). Partial pressures in this equation should have been divided by a reference pressure value. This is important not only for dimensional consistency, but also to discern between the pressure value actually adopted in simulations from that originally used as reference in the derivation of Eq. (4.56l).
- ix. As it appears, there is a critical error in Eq. (4.56h) when one inspects the definition given by Eq. (4.56k). As discussed in §§2.3, the polarization “ η ” in this case must be the activation polarization (η_{act}) and not its augmented version. Therefore, in this work the authors have completely neglected Nernstian voltage losses due to concentration polarizations. One might argue that in Eq. (4.56l) the influence of concentration would have been already accounted for. In this case, however, this latter equation was obtained from the work of de Boer^[94], which was, in fact, devised for use with activation polarization. Even though the form of the BVE Eq. (4.56h) is, in principle, meant to be applied with η_{act} , as this equation is an empirically-based formulation it is possible that one could use the exchange current density formula, Eq. (4.56l), to fit experimental results based on augmented polarization values. Nonetheless, besides being a conceptual incongruity, this procedure most certainly would lead to significant errors, even within the interpolation range of experimental data.

Table 4.21: Structure resolved model from Shikazono *et al.* [91] & Kanno *et al.* [102] & Matsuzaki *et al.* [145].Combination of Governing and Constitutive “Laws” for Continua (*i.e.*, Archetype Continuum Transport Equations)

$$\nabla \cdot \left[\left(\frac{1 - \varpi_{H_2} y_{H_2}}{D_{H_2, H_2O}} + \frac{1}{D_{H_2}^{Kn}} \right)^{-1} \nabla C_{H_2} \right] = \dot{S}_{\mathbb{V}, C_{H_2}}$$

explanations on this equation are analogous to those provided in Table 4.20; any additional information is given in “Numerical Scheme” and “Assumptions and Remarks”.

in porous electrodes (4.57a)

$$\varpi_{H_2} = 1 - \left(\frac{M_{H_2}}{M_{H_2O}} \right)^{1/2}$$

in porous electrodes (4.57b)

$$\nabla \cdot \left(\frac{\sigma_e}{\mathcal{F}} \nabla \tilde{\mu}_{e^-} \right) = \dot{S}_{\mathbb{V}, \tilde{\mu}_e}$$

in porous electrodes (4.57c)

$$\nabla \cdot \left(\frac{\sigma_{io}}{2\mathcal{F}} \nabla \tilde{\mu}_{O^{2-}} \right) = \dot{S}_{\mathbb{V}, \tilde{\mu}_O}$$

in porous electrodes (4.57d)

Source Terms

$$\dot{S}_{\mathbb{V}, C_{H_2}} = \begin{cases} \frac{i_0 \lambda_{tpb}}{2\mathcal{F}} \left[\exp \left(\frac{2\mathcal{F}}{\mathcal{R}T} \eta_{act} \right) - \exp \left(-\frac{\mathcal{F}}{\mathcal{R}T} \eta_{act} \right) \right] & , \text{ at the TPB} \\ 0 & , \text{ elsewhere} \end{cases} \quad (4.57e)$$

$$\dot{S}_{\mathbb{V}, \tilde{\mu}_e} = -2\mathcal{F} \dot{S}_{\mathbb{V}, C_{H_2}}$$

in porous electrodes (4.57f)

$$\dot{S}_{\mathbb{V}, \tilde{\mu}_O} = 2\mathcal{F} \dot{S}_{\mathbb{V}, C_{H_2}}$$

in porous electrodes (4.57g)

$$\eta_{act} = -\frac{1}{2\mathcal{F}} \left\{ 2 \tilde{\mu}_e^{TPB} - \tilde{\mu}_{O^{2-}}^{TPB} + \left[\Delta G^\circ + RT \ln \left(\frac{p_{H_2O}}{p_{H_2}} \right) \right]_{RE} \right\}$$

in porous electrodes (4.57h)

CONTINUATION OF TABLE 4.21

$i_0 = 31.4 \times p_{H_2}^{-0.03} p_{H_2O}^{0.40} \exp\left(-\frac{1.52 \times 10^5}{T}\right)$	in porous electrodes	(4.57i)
Lattice-Boltzmann Method (“Numerical Scheme”)		
$f_i^{eq} = \frac{1}{6} \sum_{i=1}^6 f_i(\mathbf{x}, t) \quad (\text{D3Q6 model is also used in this work})$	in porous electrodes	(4.57j)
In this work, differently from Table 4.20, the relaxation time τ_c is expressed as a function of diffusion coefficient, voxel size Δx , and time step Δt :		
$\tau_c = 0.5 + \frac{3 D \Delta t}{(\Delta x)^2}$	in porous electrodes	(4.57k)
Where the mass diffusion (“DGM”) coefficient is given by (see Eq. (4.57a) above)		
$D = \left(\frac{1 - \varpi_{H_2} y_{H_2}}{D_{H_2, H_2O}} + \frac{1}{D_{H_2}^{Kn}} \right)^{-1}$	in porous electrodes	(4.57l)
Assumptions and Remarks		
<p>i. Similarly to the work of [286], described in Table 4.3, Eq. (4.57a) may be seen as a result from DGM and which is valid for the case of isobaric counter-diffusion (uniform total pressure). Said more correctly, this equation follows directly from the Modified Maxwell-Stefan Model and not from DGM, assuming the validity of Graham’s “Law”. In this model, the Bosanquet formulation is also implied. The Knudsen diffusion coefficient was evaluated as in the previous work (Table 4.20) and also assuming a constant mean pore radius (0.75 μm) in all simulated cases.</p> <p>ii. Differently from their previous work, Shikazono <i>et al.</i>^[91] solved transport equations for electrochemical potentials of electron and oxide ion (Eq. (4.57c) and (4.57d), respectively). Details on how electric potentials and polarizations values are recovered from electrochemical potentials can be found in the above mentioned paper.</p> <p>iii. Note that in Eq. (4.57e)-(4.57g) the sign of source terms has changed. There are two reasons for that:</p> <ol style="list-style-type: none"> There was a change in the orientation of coordinate axes. In the previous work^[335], the positive direction of main reaction axis (x-axis) was oriented towards the electrolyte interface. However, in this work the positive direction of reaction axis (in this case the z-axis) is now oriented towards the current collector layer, so in the opposite direction. The sign change is necessary in order to maintain physical consistency of state variable gradients (<i>i.e.</i>, the flux should be directed down the gradient field). Previously, equations governing the charge conservation were written in terms of electric potentials, whereas in this work the authors have opted to use electrochemical potentials. In this latter case, negative electric charges account for the change in sign (see Eq. (2.42)). <p>iv. The BE, Eq. (4.57e), now uses the activation polarization (η_{act}) according to the definition of Eq. (4.57h), instead of the augmented overvoltage. The error in their previous work was therefore corrected (see note “ix” in Table 4.20). The subscript “RE” used in Eq. (4.57h) stands for “reference electrode”, whose hypothetical surface is assumed to be in thermodynamic local equilibrium with the gaseous (gas bulk) phase. This definition of Eq. (4.57h) is formally equivalent to that of Eq. (2.29).</p> <p>v. In this work Shikazono <i>et al.</i>^[91] defined the relaxation time (τ_c) explicitly, according to Eq. (4.57k). Here the authors indicated that the time step Δt was chosen so that the relaxation time becomes $\tau_c = 0.99$. However, as the “DGM diffusion coefficient” (see Eq. (4.57l)) is not constant within the gas-phase, the time step should be changed accordingly.</p>		

CONTINUATION OF TABLE 4.21

- vi. The work of Kanno *et al.*^[102] applied the same modeling equations of Shikazono *et al.*^[91], with some distinctions. They are:
 - a. The authors have incorporated another model for evaluating the exchange current density i_0 : in addition to de Boer's model^[94], as per Eq. (4.57i), they have also considered an exponential equation fitted on experimental data from Bieberle *et al.*^[371] for comparison purposes.
 - b. Although the relaxation time (τ_c) was calculated using the same equations, Eq. (4.57k) and (4.57l), there is a slight difference concerning the time step Δt . Kanno *et al.*^[102] chose Δt so that the relaxation time results $\tau_c = 0.99$ at the point where the diffusion coefficient D takes its maximum value.
- vii. Matsuzaki *et al.*^[145] applied very similar models to those of Shikazono *et al.*^[91] and Kanno *et al.*^[102]. In the case of Matsuzaki and coauthors the used equations have a number of obvious differences stemming from the fact that a different type of problem was considered in their work (*i.e.*, the modeling of a MIEC cathode instead of *Ni*-YSZ composite anodes). A specific modification worth mentioning concerns the expression used to evaluate the relaxation time in the LBM: $\tau_c = 0.5 + D\Delta t/[3(\Delta x)^2]$. Thus one sees that the factor “3” is now in the denominator when compared to Eq. (4.57k). It is not clear, however, whether this was a typographical error or not, as there was no written argument for such modification.

4.6.2.2 Joshi, Chiu, and Coauthors

Researchers from The University of Connecticut have developed LBM simulations^[372, 373, 338, 374] to study 2D and 3D mass diffusion of both reacting and inert species in the pore space of *Ni*-YSZ anodes. For 3D simulations, the authors used computational domains constructed from both real (reconstructed via XCT) and virtual samples of porous electrodes, the latter based on 3D material models constructed via sphere packing algorithm. For 2D simulations, geometry input data from a single micrograph (SEM) image was used in conjunction with periodic boundary conditions along one of the two main coordinates axes (in order to represent the total extents of the original electrode layer; see Figure 4.7 for clarifications). The main goal in these works^[372, 338] has been to develop a multicomponent mass transport model to obtain the steady-state mole fraction distributions of reacting (H_2 , H_2O) and inert (N_2) gases throughout the porous anode (see Fig. 4.7). This information was used to evaluate the effect of medium geometry (mainly the porosity) and to calculate the anodic concentration polarization. A secondary goal was to determine structural (porosity-tortuosity) factors ψ_{str} of reconstructed 3D geometries, by solving the 3D Laplace equation for a “generic conserved quantity” (see [338] for details). Calculated factors were then used in 1D macro-homogeneous models employing effective diffusivity values (as in, for example, the model given in Table 4.4), to simulate the same multicomponent mass transport problem. Finally, respective results were compared to those from the structure-resolved (LBM) simulation.

In terms of physical modeling considerations, the markedly differences of the works of Joshi and coworkers in comparison to that of tables 4.20 and 4.21 are: (i) Joshi and coworkers considered a true multicomponent mass transport (*i.e.*, ternary gas system), whereas researchers from the University of Tokyo solved the mass diffusion problem for only one gas component (*i.e.*, H_2); (ii) differently from the models in tables 4.20 and 4.21, Joshi and coworkers treated the TPB region as an infinitely thin boundary (located at anode/electrolyte interface) and thus without the precise spatial identification of TPB regions through the anode thickness; (iii) as a direct result of (ii), Joshi and coworkers have also not considered the simultaneous modeling of electron transport (through the *Ni* phase) and ion transport (through the *YSZ* phase). Nonetheless, the multicomponent mass transport model developed by Joshi *et al.*^[373] has a higher physical fidelity and relies on less simplifying assumptions. Their LBM variant is based on the two-fluid model initially proposed by Luo and Girimaji^[375] and extended by McCracken and Abraham^[376] in order to model gas components with different molecular weights. Even though Joshi and coworkers have discussed elsewhere (*e.g.*, see [377]) about the capability of LBM in describing non-continuum diffusion effects, this topic was not the focus of their SOFC simulations^[372, 373, 338], wherein they focused on continuum transport modeling only. The actual mathematical model proposed by these authors will not be presented in this section, as this would require an overly lengthy discussion of LBM, unfit for the purposes of this chapter.

Figure 4.7: porous SOFC anode model from Joshi *et al.*^[373] used in 2D LBM simulations. Also shown are simulation results of mole fraction distributions for H_2 and H_2O for the case where $\varepsilon = 0.5$ (figure by the author).

4.6.2.3 Paradis and Sundén

Paradis and Sundén^[346] evaluated the application of LBM for modeling reaction-diffusion processes in a porous SOFC anode on a mesoscopic level. These authors applied the modeling framework of Joshi and coworkers^[372, 373], with the apparent difference being that Paradis and Sundén considered a binary gas mixture (H_2 and H_2O). They also performed LBM simulations in 2D porous domains: one of the porous domains was created through randomly placed circular obstacles; and the other one was obtained by discretization of a single micrograph image of a real anode sample. By studying different simulations scenarios, with and without including the production and consumption of chemical species (*i.e.*, electrochemical reactions), Paradis and Sundén aimed at the evaluation of geometry effects as a “potential risk” for limiting transport processes (“transport blockage”). Although there are not much supporting results or discussion in their paper, these authors were probably interested in highlighting that currently used macro-homogeneous models might not be capable of evaluating microstructure effects of porous SOFC anodes. In other words, that with a few empirical macroscopic parameters (*e.g.*, porosity and tortuosity) one cannot properly describe the effective interaction between fluid particles and walls of the porous media, and thus to capture the mesoscopic physical behavior.

4.6.2.4 Guan *et al.*

Guan *et al.*^[351] applied the modeling framework of Joshi and coworkers to simulate gas transport in *Ni-YSZ* 3D microstructures subjected to thermal cycling treatments. Thermal cycling treatments strongly influence the anode 3D structure, including interior connectivity, phase size, and TPB density. After each thermal cycle, the authors calculated the concentration polarization based on the simulation results of mole fraction distributions of electroactive species, through the connected pore phase. Even though Guan *et al.* have obtained a (experimental) 3D detailed distribution of TPB sites (from XCT reconstructed microstructures samples), they chose a simplified distribution model of TPBs, akin to the work of Joshi *et al.*^[372], where TPB regions were treated as zero-thickness boundary, located at the anode/electrolyte interface. It is worth noting an erroneous statement made in the paper of Guan *et al.*^[351]: the authors stated that the LBM is improper for gas transport modeling when the pore diameter is smaller than the mean free path of the gas molecules (*e.g.*, when “diffusion” is dominated by molecule–wall interactions); and that, in this case, LBM should be replaced by other methods. The literature is vast enough (though largely ignored by the SOFC community) with respect to works that use LBM in nanoporous materials or in other flow systems with rarified effects. Surely, the LBM version that was applied by Guan *et al.* is

unsuited for this task, but this does not mean LBM is definitely unable to model the intermediate regime, encompassing free molecular flows. Certainly, strong non-equilibrium flows cannot be properly described by theories based on standard Boltzmann equation^[174, 378] and, therefore, through hierarchically derived models such as the LBM.

4.6.2.5 Xu *et al.*

Xu *et al.*^[329, 379] performed LBM simulations on the mesoscale to emphasize the capabilities of this modeling technique for the accurate prediction of multi-component mass transfer in SOFC porous electrodes, especially when it is compared to traditional approaches such as macro-continuum models. Furthermore, despite the frequently assumption made in some SOFC modeling approaches, which ignores the concentration polarization (*i.e.*, assumes that the gas transport in SOFC electrodes is a “very efficient process”), these authors discuss that multi-component mass transfer in porous electrodes can have profound effect on the simulation of the cell electrochemical performance. More precisely, Xu and coauthors indicate that concentration polarization can reach the same order of magnitude as the other two main polarizations (“activation” and “ohmic”) for the cases of low porosity, low reactant concentrations, and high average current densities. Therefore, they conclude that to simply neglect the concentration loss is unreasonable based on the account that reactant concentration and current density vary sharply along the flow channel of fuel cell^[329]. Meanwhile, these authors also affirm that some classical macroscopic models (*e.g.*, based on MFM, DGM, and MSM), which have been used to evaluate concentration polarization, might as well result in imprecise prediction of SOFC losses, given that they are not competent to study the gas transport accurately in porous electrodes on the micro or mesoscale. Or, at least, Xu and coauthors have shown that LBM can be a much more accurate method for simulating mass transfer within SOFC electrodes.

Xu and coauthors used a representative elementary volume (REV) scale Lattice-Boltzmann (LB) model based on the Brinkman-like equation for flows in porous media. Compared to other the pore scale models (including most of LBM models mentioned in the above paragraphs), in which detailed geometric information is needed and the computation domain cannot be too large due to limited computational resources, the REV scale LB model can be used for systems of larger size and it is more competitive in parametric studies. Several LBM models in SOFC literature has either adopted single-fluid models (employing single relaxation time approximation, which is restricted to unity Prandtl and Schmidt numbers^[369] or has taken the species concentration field as mere a passive scalar. Similarly to Joshi *et al.*^[373], Xu and coauthors implemented^[329] a two-fluid model, which treats mutual collisions and self-

collisions independently so that the viscosity and diffusion coefficients can be varied independently by a proper choice of mutual- and self-collision relaxation-time scales. The authors have applied the REV scale LB model in 2D simulations to investigate the transport of multi-component reactant gases and to study electrochemical characteristics of a planar anode-supported SOFC^[379]. As for the case of Joshi *et al.*^[372, 373], the actual mathematical model proposed by Xu and coauthors will not be presented in this section, as this would also require an overly lengthy discussion of LBM.

4.6.2.6 Determination of Effective Transport Properties

Finally, there are works in the SOFC literature that solved continuum transport equations (the same as those presented in §4.5.2) on the pore-scale, using well-known methods such as finite-difference method^[341, 354], finite-volume method^[356], finite-element method^[344], and volume of fluid method^[333]. Essentially, the goal of these works has been to predict physical properties by solving discretized partial differential equations without source terms (e.g., Laplace equation). Since boundary conditions are identical for the equivalent macro-homogeneous material and the real sample material, the pore scale solution (e.g., local concentration distribution or its resulting mass flux evaluated at the boundaries of the domain) is then compared to prescribed macroscale mass fluxes in order to calculate effective transport properties (e.g., effective diffusion coefficient). For instance^[341],

$$D^{\text{eff}} = \frac{\xi_{i,\text{max}}}{S_n (\theta_1 - \theta_2)} \iint_{\mathbb{S}} \left(-D_{\text{voxel}} \frac{\partial \theta}{\partial \xi_i} \right) dS_n \quad (4.58)$$

where in Eq. (4.58): θ represents some conserved quantity (e.g., species concentration); ξ_i corresponds to either x , y or z (along the sample volume axes); $\xi_i = 0$ for $\theta = \theta_1$ and $\xi_i = \xi_{i,\text{max}}$ for $\theta = \theta_2$ are fixed boundary conditions; S_n is the surface area normal to the flux (i.e., $dS_n = \vec{n} \cdot d\vec{S}$, where $\vec{n}$ is the outward pointing unit normal field of the sample's boundary); D_{voxel} is the (local) bulk diffusion coefficient (depending on the phenomenon, it can be either heat conductivity, electronic or ionic conductivity, or mass diffusivity), characteristic of the phase present in the considered voxel. Here again the reconstructed material enters the simulation after its voxelization and it is thus described as a set of rectangular or cubic of voxels. The numerics are performed on equidistant variables at the voxel centers. Within each voxel, D_{voxel} is assumed constant. The quantity $\theta = \theta(x, y, z)$ is the solution obtained from the discretized partial differential equations that were solved within the reconstructed (voxelized) sample material, in a preceding step.

4.7 Multiscale Models I: Macroscale Models Informed by Microscale Correlations

In a brief, macroscale models informed by microscale¹⁷ correlations are simply those models already discussed in §§4.5.2, but which employ partially-resolved models of porous electrodes (see §§4.6.1) to evaluate the required effective transport properties. These models are more commonly applied in parametric studies, when one is particularly interested in assessing, on a straightforward manner, the effects of certain micro-geometry parameters (e.g., electrode particle size) on macroscale variables (e.g., current density and cell voltage). This type of modeling technique may be included within the so-called “hierarchical multiscale approaches”, in which known information at one scale, typically passing through some sort of averaging process, is used to generate a model on a larger scale. A listing of reference works that have applied the above mentioned technique is provided in Table 4.22 (some these references were already cited in other sections of this chapter).

Table 4.22: Macroscale models of SOFC porous layers Informed by microscale correlations.		
Based on DGM	Based on MFM or EPDM	Based on MMS
Bertei <i>et al.</i> [367] Bertei <i>et al.</i> [334] [♦] Bertei <i>et al.</i> [85] ^{♦♦} Chen <i>et al.</i> [380] [♦]	Nam and Jeon [366] Liu <i>et al.</i> [381] [♦] Hosseini <i>et al.</i> [382] [*] Wang [383] [♦] Wen <i>et al.</i> [137] ^{♦*} He <i>et al.</i> [384] ^{♦♦}	Chinda <i>et al.</i> [385] [*]
Notes: ♣: Mass transport equations used in this work have critical errors; some are similar to those pinpointed in §§4.5.2. ♠: Work that also discuss the influence of the variability of modeling parameters on cell performance. *: The only work in the literature to model the effect of interfacial strain on gas transport properties. ♦: Noteworthy work.		

4.8 Multiscale Models II: Macroscale Models Informed by Microscale Simulations

It may seem contradictory, but several of the works reviewed in §§4.6 (“single-scale models on the mesoscale”) are also, in some sense, what one may refer to as “macroscale models Informed by microscale simulations”. That is, although they solve transport equations on a characteristic mesoscale length (“geometrical mesoscale”), part of the physics that are captured by the modeling equations are not on the mesoscale but on a coarser-scale. Therefore, the claims of some of those works of having performed “fully mesoscale simulations” are not, rigorously, a true assertion. From the perspective that transport

¹⁷ Here the term “microscale” is used loosely, meaning everything that is “smaller” than the macroscale.

phenomena have been solved in the pore-level description (mesoscale length) those works have indeed simulated, at least partially, mesoscale phenomena. However, as most of the governing (and/or constitutive equations) have been expressed under the hypothesis of a continuum medium (e.g., for which the validity of the hydrodynamic limit is implied), they also incorporate some of the limits that constrain the macroscale-continuum description. Furthermore, the use of LBMs based on a single relaxation time is another example of such limitation^[386, 387, 388].

Therefore, at this point one may acknowledge that all representative works from the SOFC literature that applied “macroscale models Informed by microscale simulations” have been considered in preceding sections. There is but one example that is worth (re)mentioning and that should be taken as representative of the class of simulations that indirectly, or non-concurrently (see §§4.9 for clarification on this term), use microscale information to simulate macroscale processes. These models (“macroscale models informed by microscale simulations based on 3D reconstructions”) are conceived in a similar fashion to those described in §§4.7 (“hierarchical multiscale approach”), but with the fundamental difference related to how microstructural parameters (“the passing information”) are quantitatively evaluated. In this case, these parameters (whether purely morphological or not) are obtained through direct numerical simulation on the geometrically complex pore-scale, which was topographically reconstructed from FIB-SEM or XCT measurements. The information gathered from the pore-scale simulation is then averaged to the appropriate macroscale characteristic length, using some suitable homogenization method (as, for example, the one mentioned at the end of §§4.6.2). Once microstructural parameters have been quantified, they are used in 1D (or, sometimes, in 2D) macroscale simulation of SOFC electrodes.

A representative example of such modeling technique, which indirectly use microscale information to simulate macroscale processes, is that of Kishimoto *et al.*^[342] who have quantified microstructural parameters (e.g., volume fractions, tortuosity factor, surface-to-volume ratio, and TPB density) by means of random-walk-based diffusion simulations. The quantified parameters were then applied in the 1D macro-homogeneous numerical simulation of a *Ni-YSZ* cermet, using the DGM to evaluate the mass transport. Other examples from literature that applied this modeling technique were already presented in this chapter^[373, 328]. These works all have implemented 1D macro-homogeneous models as a basis of comparison with 3D mesoscopic models of electrode performance. However, in their assessment of one-dimensional models, the respective discussions were relatively narrow in scope. In the aforementioned works, microstructural parameters have been obtained as fixed values, without the possibility to link these values to the changes of microstructure features (e.g., in contrast to

the micro-modeling models of Table 4.19) unless a new full simulation on the pore-scale is performed. This possibility would confer a significant flexibility to their usage and also enrich the discussion on how these models compare to 3D mesoscopic models. By the time of this writing, there is no published work in SOFC literature that derives expressions to upscale individual pore performance to full-scale electrodes¹⁸. Furthermore, most published works have only resorted to “full homogenization” (*i.e.*, a single parameter value is attributed to porous layer as a whole¹⁹) and none of them has applied more sophisticated (*i.e.*, more rigorous) upscaling techniques, such as those based on the method of volume averaging^[389, 390, 48, 391].

4.9 Multiscale Modeling: Principles, Multiscale Homogenization, and Hybrid Methods

This section address some topics that are deemed important to clarify key concepts of multiscale modeling, particularly within the context of the so-called “macroscale models Informed by microscale simulations”. The present dissertation work is not, in fact, about multiscale modeling techniques *per se* or bridging-scale methods^[154, 155, 39]. However, by briefly examining some of the principles and methods of multiscale modeling, this monograph can certainly emphasize the potential deficiencies of current SOFC mathematical models used to simulate mass transport processes. Several of these deficiencies are related to whether or not perform microscale or mesoscale simulations according to local (microscopic and mesoscopic) quantities instead of using macroscale-continuum constitutive relations. That is, in what conditions one should calculate macroscopic properties of materials by theoretical modeling and computational simulation from a more fundamental perspective. This “inescapable” necessity of modeling physicochemical processes on disparate scales, in order to accurately evaluate large-scale phenomena, has been suggestively referred to as “the tyranny of scales”^[392] because it is not an easy task to recognize the aforementioned conditions. Moreover, no single solution or approach has the potential of bridging all dissimilar scales^[154, 155] in to a seamless description.

¹⁸ The work of Bertei *et al.*^[334] would be the closest to this goal. As an example of what is meant by “expressions to upscale pore-scale performance,” see Blasi *et al.*^[420] who have modeled reaction–diffusion processes within catalyst washcoats.

¹⁹ Nishi *et al.*^[328] seems to be an exception. These authors also applied a 1D model with local values for the tortuosity factor (*i.e.*, the value of this parameter varied according to the distance from the electrolyte interface). The model gave poor results when compared to the one that used averaged tortuosities (*i.e.*, a single parameter value).

Multiscale modeling is a wide-ranging interdisciplinary field, where approaches are often material- and application-specific. The use of any multiscale approach has to be carefully weighed on a case-by-case basis^[155]. According to Fish^[154], multiscale modeling should take advantage of the fact that in many natural systems only a small fraction of the total region is of interest. Determining which regions should be simulated with coarse-scale²⁰ or fine-scale models really improves the odds of minimizing the above mentioned deficiencies. Outside of the region of interest one should only perform coarse-scale calculations, because no detailed information about this region is necessary. Whereas in the region of interest one should perform both fine-scale and coarse-scale calculations: the coarse-scale describes the homogeneous part of physicochemical processes using just a few degrees of freedom; on the other hand, the solution of fine-scale equations enables the detailed modeling of physicochemical processes and thus higher fidelity where it is necessary. Therefore, by considering simultaneously models on different scales, the aim is to select a multiscale approach that effectively shares the efficiency of macroscopic models as well as the accuracy of microscopic models^[39]. Multiscale approaches may be subdivided in two categories^[155]:

- I. Information-passing (or hierarchical) multiscale approach: in this approach, the fine-scale response is idealized (*i.e.*, approximated or unresolved) and its overall (average) response is incorporated into the coarse-scale description. Information-passing methods are typically used to model the overall response of fine-scale phenomena, except at the so-called “hot spots”, *e.g.* in the vicinity of boundary-layers, where concurrent methods are more suitable. The quantities of interest are limited to the coarse-scale, provided that they can be readily computable from fine-scale information. Special features of the fine-scale physics (*e.g.*, scale separation and self-similarity) should be taken advantage of.
- II. Concurrent multiscale approach: fine and coarse-scale resolutions are simultaneously employed at different portions of the problem domain (in some modeling contexts, this approach is also known as “hybrid method”) and the exchange of information occurs through their interface. Thus, the concurrent multiscale modeling performs simultaneous simulations at different spatio-temporal scales within a single simulation process, in which there is dynamic sharing of information between concurrent simulations. Computational subdomains, where different scale resolutions are employed, can be either disjoint or overlapping.

Concurrent approaches require that precise information on the material microstructure should be known in subdomains where fine-scale models are to be considered. Moreover, the interface (or interphase) between the fine and coarse scales should be properly described. Thus, the utilization of concurrent methods is, in practice, hindered when there is a lack of

²⁰ From the point of view of statistical mechanics, coarse-scales are those that can be observed directly in experiments and only the averaged effects (ensemble averaging) of fine-scales quantities are important.

detailed knowledge about the microstructure at “hot spots”. At these locations, concurrent multiscale approaches require fine-scale resolution whereas information-passing approaches only require the material microstructure to be reconstructed in small representative “windows” (*i.e.*, from a REV sample). Another formidable roadblock to concurrent approaches is the uncertainty and complexity introduced by the physics of finer-scales, which requires the (prior) identification of what information need to be transferred from one model or scale to another and what physicochemical principles must be satisfied during the transfer of information^[154]. Thus, when coupling coarse and fine scales one has to account for the different fundamentals of each theory (*e.g.*, whereas in the theory of molecular dynamics every individual molecule is considered, in the continuum mechanics an average is considered) and how to properly describe the transition (or the so-called “handshaking”) region that actually bridges both theories.

In both information-passing and concurrent approaches, the overall response of the material from its fine-scale constituents can be obtained using homogenization techniques^[155, 389, 391]. Among the necessary conditions for homogenization of a multiscale system, one requires that, at a certain finer scale, the governing equations, including the constitutive equations of physical phases, are well understood or, at least, better understood than at the coarser-scale^[154]. Under this assumption, homogenization establishes a mathematical framework by which coarse-scale equations can be derived from well-defined fine-scale equations, provided that spatial scales are separable at all relevant scales. However, the variability of physicochemical parameters at multiple scales might affect the medium homogenization and thus the simulation outcome. For instance, microcracks are often randomly distributed and characterization of their interface properties is difficult. In this case, the use of a multiscale approach may not be the best choice. Nevertheless, novel multiscale techniques, such as the multi-resolution continuum approach^[393] can cope with the above difficulty by incorporating statistical factors into the mathematical model. The multi-resolution continuum approach is based on the concurrent nested homogenization of the randomness of material structures.

Information-passing and concurrent multiscale approaches are two alternative (and complementary) modeling techniques that constitute what was referred to as “macroscale models Informed by microscale simulations”. The SOFC literature that has been reviewed in this dissertation has no examples in which the concurrent multiscale approach was effectively applied. Furthermore, a number of works that have allegedly performed fine-scale simulations (as in §§4.6) are affected by possible inconsistencies between the length scale on which simulations have been executed and the theoretical basis that limits the physical validity of the

respective modeling equations. These inconsistencies may be seen as a manifestation of the limits for the spatial and temporal scales within which the “true” governing physics is valid. The physics governing transport processes often changes with scale, so that the models themselves must change in structure as the numerous ramifications of transport-related events pass from one scale to another. Therefore, the correct description for the applicable scaling physics can dominate simulation efforts wherever large disparities in spatio-temporal scales are encountered^[392].

4.10 Reactor (Gas Channel) Models

4.10.1 Button-Cell Reactor and Impinging Wall Jet Flows

As the main topic of this work is the discussion of gas transport within the porous layer of SOFCs, only succinct remarks are made in order to highlight a number of possible shortcomings of simplified mathematical models that are used in gas channels. Moreover, as introduced in §§1.4, only the button-cell flow arrangement is considered herein. Nevertheless, much of the discussion in this section is general enough to be valid for other types of channel geometries. The importance of properly modeling gas channels has been already discussed in this chapter: the main goal of this model is, within the overall simulation setup, to account for the effect of fuel (or oxidant) depletion along the gas channel of a SOFC (see Fig. 3.8 and Fig. 3.9), as progressively more fuel/oxidant is utilized in the chemical reactions. Ideally, this model should capture all non-uniformities (gradients) in the concentration of gas species within the channel's volume. Thus, not just the lengthwise depletion is important but also the determination of the actual gas concentration at the channel/porous layer interface; that is, in the case where the gas concentration value in the “bulk” (far away from the wall) is significantly different from that found deep within the flow boundary-layer.

From the point of view of fluid dynamics, gas flows in button-cells (see Fig. 1.17 and Fig. 1.18) can be considered to fall within the general family of impinging wall jet flows; or, more precisely, radial wall jets^[394, 395] formed by the normal impingement of a round (or slot) jet, whose nozzle is separated from the wall by a finite distance (often called nozzle-plate spacing or just gap). The radial jet is assumed to spread over a plain, permeable wall with local suction and/or injection (depending on the “flux direction” of the net reaction rate in the porous domain). Although this type of flow has been extensively studied in the literature^[396, 397, 398, 399, 400, 401, 402, 403], works in the SOFC literature paid little or no attention to these studies. Therefore, no comprehensive review will be reported in this monograph concerning this

thematic (“impinging wall jets”). The presentation will be limited to what is typically considered in the SOFC literature.

There are three alternative formulations often used for simulating the steady-state flow in gas channels for conditions that are typical of button-type SOFCs, namely: (i) Navier-Stokes equations (or CFD approach); (ii) boundary-layer equations; and (iii) plug-flow equations. Nevertheless, models based on the boundary-layer approximation have seldom been used (this author is unaware of any published work that actually applied such models to SOFCs). The discussion of these models will be in the lines of Raja *et al.*^[404], who critically evaluated similar flow models for catalytic-combustion monoliths. The remarks on gas channel models aim to draw attention to the range of validity of the various approximations in terms of physical and numerical accuracy (computational resources required to perform calculations is of less importance here).

Depending on the flow conditions, certain approximations and simplifications may be appropriate in representing the mass transport. Comprehensive models are often based on solving the complete Navier-Stokes equations (*i.e.*, CFD numerical codes), considering mass and momentum transport along both radial and axial directions. Plug-flow models are relatively simpler models that disregard diffusive terms, forming a differential-algebraic-equation (DAE) initial-value problem for the axial variation of the “mean” species composition. An intermediate alternative is to use models based on the boundary-layer approximation, wherein axial (stream-wise) diffusive transport is neglected, but detailed transport to and from channel walls is retained (including diffusion). In this case, boundary-layer equations can be casted into a system of DAEs (for instance, using the method of lines).

Beyond assuming perfect-gas behavior and laminar regime, Navier-Stokes equations (the CFD approach) used in the SOFC literature have few assumptions. Their solution, when solved in conjunction with mass-species transport equations (*e.g.*, Fickian models), provides axisymmetric velocity, pressure, and species composition fields in the channel (see Fig. 4.8 as an example of CFD solution in a button-cell). There are several numerical studies that have used CFD models to calculate the flow in the gas channels of button-type SOFCs^[31, 405, 304, 406, 407, 408, 409]. Particularly, in Fig. 4.9 it is shown the CFD solution obtained by Goldin *et al.*^[304] for the H_2 mole fraction along the button-cell symmetry axis (fuel chamber). In this case, one can verify that the concentration gradient, along the normal direction to the wall, was in fact negligible at different testing conditions of current density and fuel flow rate. However, as will be seen below, this may not be always the case (*e.g.*, mass-transfer limited reactions) depending on channel geometry and cell operating conditions (*e.g.*, reaction rates, flow rates, fuel/oxidant dilution ratio).

Figure 4.8: CFD simulation by Suwanwarangkul *et al.*^[405] inside of a fuel channel: (a) surface and arrow plots of velocity field; surface and contour plots of concentrations for (b) H_2 and (c) H_2O . Simulated conditions: $E_{cell} = 0.7$ V; $T = 1173$ K; gas composition at inlet 20% H_2 , 20% CO , 14% CO_2 , 3% H_2O , and 43% N_2 .

Figure 4.9: CFD simulation performed by Goldin *et al.*^[304]: H_2 mole fraction along button-cell axis in the fuel chamber and within the anode layer. Solutions are shown for two fuel flow rates: (a) 200 sccm; and (b) 25 sccm.

4.10.2 Simplified Models (PFR, SFR, RFR)

Comparative results^[404] indicate that the boundary-layer and Navier-Stokes models are in good agreement over a wide range of flow conditions. The plug flow model, however, must be used with caution. Under some flow conditions, when chemical reactions are mass-transfer limited, plug-flow models can significantly overpredict the conversion rates of fuel and/or oxidant. Thus, in some situations, the range of applicability of these models is critically limited if accuracy is sought to be achieved. Still according to Raja *et al.*^[404] the validity of the boundary-layer approximations improve as the Reynolds number increases. Under these circumstances, the axial diffusive transport is diminished in comparison to the radial diffusion and convective transport. On the other hand, as Reynolds number decreases, the stream-wise diffusion strengthens relative to convection. Mathematically, the character of the governing equations would change from parabolic to elliptic and, in this case, the accuracy of the boundary-layer approximation can be expected to decrease. Latter in this section, two boundary-layer models will be shortly addressed, namely the radial flow reactor (RFR) and stagnation flow reactor (SFR).

4.10.2.1 Plug-Flow Reactor Model (PFR)

Plug-flow equations (plug flow reactor model or just PFR) eliminate all diffusive terms and therefore any boundary-layer physics. In the axial direction, diffusion is assumed to be small compared to axial convective transport (much the same assumption as in the boundary-layer approximation). In the radial direction, however, diffusive transport (“crosswise mixing”) is assumed to be over dominant, thereby resulting in no radial variations in species composition. The plug-flow equation of continuity for the k -th species may be written as:

$$\frac{d(\rho_g x_k u)}{dx} = \frac{\mathcal{P}_e}{\mathcal{A}_c} M_k \dot{S}_{S,C_k} = \frac{\mathcal{P}_e}{\mathcal{A}_c} M_k \left(\dot{S}_{S,C_k}^{cat} + \dot{S}_{S,C_k}^{net} + \frac{\mathcal{A}_c}{\mathcal{P}_e} \dot{S}_{V,C_k}^{bulk} \right) \quad (4.59)$$

This equation is analogous to Eq. (4.45a), with the following nuances: the molar basis ($\text{mol m}^{-2} \text{s}^{-1}$) source term $\dot{S}_{S,C_k}$ is now expressed by the sum of three source terms. The term $\dot{S}_{S,C_k}^{net}$ represents the net mass addition (or depletion) to (or from) the gas flow at wall surfaces²¹. In the case that the walls of the channel are purely catalytic substrates (*i.e.*, impermeable and without mass deposition or etching reactions), there is no net mass exchange and thus this term vanishes identically (obviously, this is not the situation of SOFC gas channels). The terms $\dot{S}_{S,C_k}^{cat}$ and $\dot{S}_{S,C_k}^{bulk}$ represent the production (or depletion) of the k -th gas-phase species by surface

²¹ The net mass exchange can arise as a result of non-catalytic surface reactions (mass deposition or etching) and from flow through permeable walls (*i.e.*, suction or injection).

and gas-phase reactions in the channel, respectively. $\dot{S}_{S,C_k}^{bulk}$ only accounts for the production (or consumption) due to homogeneous reactions within the bulk volume of gas-phase. For SOFCs, the usual case is to have $\dot{S}_{S,C_k}^{cat} = \dot{S}_{S,C_k}^{bulk} = 0$. In order to evaluate $\dot{S}_{S,C_k}^{cat}$ and $\dot{S}_{S,C_k}^{net}$, surface convection-diffusion equations can be solved on active wall surfaces with suitable coupling to the bulk species concentrations. One sees, therefore, that $\dot{S}_{S,C_k}$ is an “apparent bulk source term”: both convective and diffusive mass fluxes at the wall are converted to this apparent source term.

One should note that if the net mass flow in the gas channel is held constant (e.g., $\dot{m} = \rho_g u \mathcal{A}_c = \text{const.}$), then as the species composition changes the density and velocity will vary accordingly. If $\dot{m}$ is not constant, besides a constitutive equation of state, an extra axial momentum equation would be required in order to solve the problem (**see APPENDIX A**), rigorously speaking. In this case an additional source term, related to the net mass addition in the channel, must be added to the axial momentum equation as well. This additional “momentum source term” will be properly represented as a spurious mass source term in the equation continuity for the mean flow. Finally, it is also important to highlight that in the plug-flow model both ρ_g and u are mean values with no radial variations. That is, the PFR yields solutions that should be considered as spatially averaged in the radial direction. Thus, in order to compare plug-flow solutions with results of Navier-Stokes or boundary-layer model it is necessary to calculate radially averaged species compositions. For instance, at a given axial location the mass-weighted, radially averaged mass fraction can be calculated as^[404]:

$$\bar{x}_k = \frac{\int_0^{r_0} \rho_g u x_k r \, dr}{\int_0^{r_0} \rho_g u r \, dr} \quad (4.60)$$

According to Raja *et al.*^[404] the plug flow model tends to overpredict reactions rates (at least in the case originally studied by these authors, where only wall catalytic reactions were considered). The reason for that is the inherent, radially homogeneous “nature” (i.e., simplifying assumption) of the plug flow model, which imposes an ideally intimate interaction between gas and surface. In a realistic depiction, however, the mass boundary-layer hinders the mass transfer between gas and reactor’s wall. Mass transfer coefficients can be used within the PFR framework to represent this “resistance” to mass transfer between the active surface and the mean gas composition, improving the accuracy of the plug-flow model, Eq. (4.59). In other words, mass transfer coefficients can be used to approximate the resistance to species mass transport crosswise. Such technique is only useful when these coefficients can be determined quantitatively or reliably estimated for a range of flow conditions. Nevertheless, for problems involving complex chemistry at surfaces and relatively short channels, mass

transfer coefficients are not easily correlated^[33, 404]. For instance, Eq. (4.59) may be modified as^[404]:

$$\frac{d(\rho_g x_k u)}{dx} = \frac{\mathcal{P}_e}{\mathcal{A}_c} M_k \left(\dot{S}_{S,C_{k,s}}^{mres} + \frac{\mathcal{A}_c}{\mathcal{P}_e} \dot{S}_{V,C_k}^{bulk} \right) \quad (4.61)$$

$$\dot{S}_{S,C_{k,s}}^{mres} = \left(\dot{S}_{S,C_{k,s}}^{cat} + \dot{S}_{S,C_{k,s}}^{net} \right) = \frac{h_{mres,k}}{M_k} (\rho_{g,s} x_{k,s} - \rho_{km}) \quad (4.62)$$

where $\dot{S}_{S,C_{k,s}}^{mres}$ is the “corrected” mass source term which accounts for the effects of mass transfer resistance; $h_{mres,k}$ is the mass transfer coefficient of the k -th species; $\rho_{g,s}$ is the mixture mass density of the gas, which is evaluated at the channel surface; ρ_{km} is the radially averaged mean mass density of the k -th species:

$$\rho_{km} = \bar{x}_k \bar{\rho}_g \quad (4.63)$$

where the radially averaged density $\bar{\rho}_g$ is calculated as

$$\bar{\rho}_g = \frac{\int_0^{r_0} \rho_g r dr}{\int_0^{r_0} r dr} \quad (r_0 \text{ is the channel radius}) \quad (4.64)$$

The surface reaction rates $\dot{S}_{S,C_{k,s}}^{cat}$ and $\dot{S}_{S,C_{k,s}}^{net}$ are now calculated using the gas-phase mass fractions evaluated at the surface ($x_{k,s}$). The species mass fractions are determined from Eq. (4.62), which is, in the general case, an implicit nonlinear algebraic relationship between heterogeneous reactions rates and the gas-phase composition at the surface. It must be solved simultaneously with the mass-continuity equation, Eq. (4.61). Generally, mass transfer coefficients will be different for each species and will vary with respect to the axial position along the channel length, *i.e.*, $h_{mres,k} = h_{mres,k}(x)$. They can be determined from the “full solution” of the channel flow field (*e.g.*, obtained via CFD) or fitted from experimental data, as:

$$h_{mres,k} = \frac{N_{k,r}}{(\rho_{g,s} x_{k,s} - \rho_{km})} = \frac{M_k \left(\dot{S}_{S,C_{k,s}}^{cat} + \dot{S}_{S,C_{k,s}}^{net} \right)}{(\rho_{g,s} x_{k,s} - \rho_{km})}, \quad (k = 1, 2, \dots, \mathcal{N}_{gas}) \quad (4.65)$$

where $N_{k,r}$ is the radial component of the species mass flux at the channel wall. Mass transfer coefficients may also be represented in dimensionless form, using the species Sherwood number:

$$Sh_{d,k} = \frac{h_{mres,k} d}{D_{km}} \quad (4.66)$$

where, in this case, the channel hydraulic diameter (d) was used as the characteristic length scale for the mass transport process. It is expected that Sherwood numbers attain high values

at the channel's leading edge and decrease downstream the channel, toward an asymptotic value^[404].

The high initial value of $Sh_{d,k}$ is associated with the very thin mass boundary-layer that begin to develop at the active leading edge²². For simple boundary conditions, the Sherwood number should decrease monotonically to an asymptotic value far downstream. For relatively more complex surface chemistry, however, it is unlikely that $h_{mres,k}$ possess a simple monotonic behavior. Furthermore, for high Reynolds numbers the chemistry behavior will tend to persist farther into the channel, as a result of which the Sherwood number may not approach its asymptotic value by the channel exit (*i.e.*, within the fixed channel length). A generalized correlation between the Sherwood number and nondimensional groups that characterizes the flow (*e.g.*, the reciprocal of the Graetz number) can be devised as^[397, 398]:

$$Sh_{d,k} = \frac{x}{d} c (Re_d)^a (Sc_k)^b \quad (4.67)$$

where a , b , and c are empirical parameters and the species Schmidt number may be evaluated as

$$Sc_k = \frac{\nu_g}{D_{km}} \quad (4.68)$$

Such correlation can be derived for laminar flows with constant gas-phase composition at the surface or for constant surface reaction rates^[162, 33]. However, for problems involving complex chemistry and concurrent transport phenomena is most probable that no general Sherwood number correlation can be found.

In the particular case studied by Raja *et al.*, these authors suggested the adoption of practical bounds to evaluate the range within which the plug-flow assumptions should be valid:

$$\frac{d}{L} \ll Re_d Sc \ll \frac{L}{d} \quad \text{or} \quad 1 \ll Re_L Sc \ll \left(\frac{L}{d}\right)^2 \quad (4.69)$$

Where L is a characteristic length scale of the flow problem. Some analysis is required concerning the precise definition of this length scale. If this length scale comprehends the entire channel length, then a complete “chemical reaction plus transport” event appears to occur within a very small distance from the leading edge of the channel. In this situation, concentration profiles will be nearly vertical (see, for example, Fig. 4.9), which is really what the plug-flow assumption is about (*i.e.*, good results on the scale of the channel length). on the other hand, if the region of interest lies in the vicinity of leading edge, then the axial length

²² The hydrodynamic boundary-layer begins to develop immediately as the unreacted flow enters the channel. A mass boundary-layer starts to grow as soon as mass transfer rates are meaningfully different from zero.

scale of interest will be much smaller than the channel length. In this case, the plug-flow model is expected to be rather inaccurate at this reduced length scale.

In the SOFC literature, virtually all published works that have applied the PFR to model the gas channel have disregarded the effect of mass transfer resistance and many of the remarks that have been made above. Examples to the contrary are really scarce. An exception worth noting is the work of Nagel *et al.*^[410]. These authors noted that depending on the geometry of the gas channel, the diffusion of the reacting species from the bulk gas to the catalyst surface can be slower than the actual chemical reaction. In this situation, the partial pressures of the reactants at the catalyst surface can differ significantly from that found in the bulk of gas-phase, thereby requiring that these partial pressures should be obtained from the solution of the complete concentration field, perpendicular to the gas flow. Nagel *et al.* proposed an alternative approach to avoid solving the corresponding full set of partial differential equations, in which a mass transfer analogy is used to compute the reactant partial pressure at the catalyst surface:

$$\dot{S}_{S,C_k} = h_{x,\text{diff-reac}} \frac{(p_x)^\alpha}{\mathcal{R} T_{\text{wall}}} \quad \text{with} \quad h_{x,\text{diff-reac}} = \frac{h_{x,\text{diff}} h_{x,\text{reac}}}{h_{x,\text{diff}} + h_{x,\text{reac}}} \quad (4.70)$$

$$h_{x,\text{reac}} = \left(\dot{S}_{S,C_{k,s}}^{\text{cat}} + \dot{S}_{S,C_{k,s}}^{\text{net}} \right) \frac{\mathcal{R} T_{\text{wall}}}{(p_x)^\alpha} \quad (4.71)$$

$$h_{x,\text{diff}} = Nu \frac{D_{km}}{d} \left(\frac{p}{p - p_x} \right) \quad (4.72)$$

where p_x is the partial pressure of the diffusion-limited specie; α is the chemical reaction order associated with the diffusion-limited specie; Nu is the Nusselt number obtained from an suitable correlation^[396, 399, 402] for the for the geometry and flow conditions considered.

4.10.2.2 Boundary-Layer Models: Radial Flow Reactor (RFR) and Stagnation Flow Reactor (SFR)

The so-called radial flow reactors or RFR^[33] are a class of chemical reactors, widely used in different scientific and industrial segments. A prominent example of this class is the chemical-vapor-deposition (CVD) reactor (axisymmetric, finite-gap stagnation flow reactors are also recurrently used to model CVDs, depending on their specific design). In these reactors, process gases flow radially outward (or inward) across parallel plates, *i.e.*, “radially diverging (or converging) flow between parallel discs”. The different designs of this type of reactor may be studied as radial variations of Jeffery-Hamel flows^[411, 33], because the application of the Jeffery-Hamel similarity represents an often used mathematical simplification of the relatively more complex 3D flow in real production reactors. In the specific case of button-type SOFCs,

depending on the geometrical design parameters of the fuel channel, the RFR model might be used to approximate the flow conditions of the system. In the SOFC literature there are few studies^[412, 413] that have made use of experimental setups resembling the radial flow reactor. Nevertheless, the respective numerical simulations of these setups, when available, have been accomplished either by means of plug-flow model^[414] or, more recently, using CFD approach^[415].

Stagnation flow reactor (SFR) models^[33] seldom have been used by the SOFC community to simulate button-cells^[416]. The practical application of these models is more common in the simulation of CVD or catalytic combustion bench reactors^[417, 34, 418]. The SFR model can be viewed as a similarity reduction of flow equations in a boundary-layer, in which the governing and constitutive equations reduce to systems of ODE boundary-value problems. What is particularly interesting to note is that, similarly to what is addressed in this section, in these other fields (e.g., modeling of CVD processes) there has been discussions on the limitations of generally employed models^[417] for properly describing the physics that occurs within the gas channel, depending on the experimental configurations employed. Moreover, how the combination between experimental configurations, operating conditions (that, for instance, can lead to mass transfer limited chemical reactions), and unsuitable mathematical models can result in illusive conclusions, such as the “masking” of real reaction rates and kinetic parameters^[34]. That is, how mass transfer effects can mask the intrinsic reactivity at typical gas-phase conditions. Thus, depending on the specific goals of a research work, is of utmost importance verifying if more accurate models, such as those based on boundary-layer approximations, are indeed necessary and “oversimplified” descriptions, such as plug-flow models, should be abandoned accordingly.

It is relevant mention that the boundary-layer models as usually found in the literature are set for conditions wherein there is no net mass exchange in the gas-phase (e.g., the SFR model is based on the Hiemenz equations with no-slip velocity boundary condition at the wall). Thus, if one expects $\dot{S}_{S,C_k}^{net}$ to have an important effect on the boundary-layer hydrodynamics (i.e., coupling of mass transport and momentum equations), these models will need modification.

4.10.2.3 Kulikovsky’s Plug-Flow Model of a SOFC Anode

As already introduced in §4.3.2, Kulikovsky^[255] developed an analytical model that takes into account the effect of fuel utilization along the gas channel of a planar SOFC anode (see Fig. 3.8), under the assumption of plug-flow conditions. This model is based on the

framework described in §§4.3.1 and in APPENDIX A. The H_2 consumption in the channel was described by the following mass balance equation:

$$u \frac{dC_{H_2}}{dx} = -\frac{i}{2F\mathcal{H}_{ch}}, \quad C_{H_2}(x=0) = C_{H_2}^{bulk,in} \quad (4.73)$$

where $\mathcal{H}_{ch}$ is the height of the channel. This ODE was rewritten in a dimensionless form as:

$$\lambda_{stch} \hat{i}_{ovr} \frac{d\hat{C}}{d\hat{x}} = -\frac{\hat{\eta} + \hat{i} \widehat{ASR}}{\widehat{ASR} + (\hat{C}_{ref}/\hat{C})^{1/2}}, \quad \hat{C}(\hat{x}=0) = 1 \quad (4.74)$$

Using the following dimensionless variables (and scaling parameters):

$$\hat{x} = \frac{x}{L_{ch}}, \quad \hat{\eta} = \frac{\eta}{b_{ts}}, \quad \hat{C} = \frac{C_{H_2}}{C_{H_2}^{bulk,in}}, \quad \hat{i} = \frac{i}{i_{crit}}, \quad \widehat{ASR} = \frac{ASR i_{crit}}{b_{ts}} \quad (4.75)$$

where L_{ch} is the channel length; $C_{H_2}^{in}$ is the inlet hydrogen molar concentration; i_{crit} is given by $i_{crit} = \sqrt{2 i_* \sigma_{io} b_{ts}}$; the hydrogen stoichiometry λ_{stch} was defined as

$$\lambda_{stch} = \frac{2F\mathcal{H}_{ch} u C_{H_2}^{in}}{L_{ch} i_{ovr}} \quad (4.76)$$

And the overall (or area-specific) current density was evaluated as:

$$\hat{i}_{ovr} = \int_0^1 \hat{i} d\hat{x} \quad (4.77)$$

The area specific resistivity ASR accumulates all resistivities, except the anodic one, and is assumed to be independent of local cell current and thus independent of $\hat{x}$. In a similar fashion to the developments of the active layer analytical model in §§4.3.1, Kulikovsky obtained solutions for Eq. (4.73) in the limiting situations of high and low current density regimes (the author also derived their respective polarization curves). For instance, in the case of low current density, the solution of Eq. (4.73) was given as:

$$\hat{C}(\hat{x}) = \frac{1}{\widehat{ASR}^2} \left[-\sqrt{\hat{C}_{ref}} + \sqrt{\hat{C}_{ref} + \widehat{ASR} \left(\widehat{ASR} + 2\sqrt{\hat{C}_{ref}} - \frac{\hat{x}(\hat{\eta} + \hat{i} \widehat{ASR})}{\hat{i}_{ovr} \lambda_{stch}} \right)} \right]^2 \quad (4.78)$$

With $\hat{i}$ expressed by the polarization curve:

$$\hat{i} = \frac{\hat{E}}{\widehat{ASR} + (\hat{C}_{ref}/\hat{C})^{1/2}} = \frac{\hat{\eta} + \hat{i} \widehat{ASR}}{\widehat{ASR} + (\hat{C}_{ref}/\hat{C})^{1/2}} \quad (4.79)$$

This analytical model developed by Kulikovsky^[255] should provide a straightforward way to rationalize the effect of hydrogen utilization ($\mathcal{U}_f$) on the anodic polarization. This model indicates that, within both high and low current density regimes, voltage losses increase rapidly for fuel utilizations $\mathcal{U}_f$ above 80%, dramatically worsening the anode performance.

Unfortunately, however, there is a critical error in Kulikovsky's model, utterly compromising its validity. More precisely, there is error in the assumption concerning his "Eq. (44)", where the author states that the equipotential condition leads to

$$\hat{E} = \hat{E}_{rev} - \hat{E}_{cell} = \hat{\eta} + \hat{i} \widehat{ASR} = \text{constant} \quad (4.80)$$

The "equipotentiality assumption" (see §§2.2.2), however, only refers to $\hat{E}_{cell}$ as being constant and not $\hat{E}_{rev} - \hat{E}_{cell}$. Indeed, as more fuel is utilized the value of $\hat{E}_{rev}$ changes along the gas channel and this remains so even if there is no concentration polarization within the porous electrode (as has been also assumed in Kulikovsky's derivations), because $\hat{E}_{rev}$ itself is evaluated at "bulk gas conditions". That is, $\hat{E}_{rev} = \hat{E}_{rev}(\hat{C}(\hat{x}))$ and it should also have been a function of H_2O concentration, e.g., see Eq. (2.15). Thus, in this case Kulikovsky also disregarded the influence of steam concentration on both fuel utilization and SOFC performance.

Chapter 5

CONCLUSIONS AND OUTLOOK

The scope of this dissertation has hitherto been mostly limited to the critical review of existing modeling techniques, although some novel research developments and results have also been presented in **Chapter 3** (see **§§3.3**). For instance, this author's dissertation concluded from thermostatics considerations and macroscale-continuum phenomenological equations that the definition of concentration polarization, as commonly found in the literature, may contain a series of limitations. It has been also discussed the relative importance of oxygen surface ad-ions on the formation of concentration cells when it is compared to the more significant concentration gradients of gas species in the porous channels of SOFC cathodes. While the reasoning behind this discussion is coherent from the macroscopic point of view, the conclusions concerning these surface effects must still be amended. Therefore, as for now they should be regarded as thought-provoking insights into the potential influence of contact chemistry near the TPB region.

More generally, this dissertation discussed a number of issues related to the mathematical modeling of concentration polarization in high-temperature SOFCs, with focus on the relation between the rate of mass transfer of electroactive species and (possible) concentration-induced voltage losses, which may arise within the electrochemical cell as a result of transport-related limitations. In particular, this research has been motivated by the necessity of raising awareness about the theoretical limitations of existing models that are presently applied in the technical literature (above all, considering what was discussed in **§§3.6**). In other words, this work has been driven by the seemingly lack of consistency among governing equations and constitutive relations, specifically those that are based on a phenomenological macroscale-continuum setting. In doing so, this work tried to show that the majority of SOFC numerical simulations performed to date, concerning concentration polarization, ignore model checking as a critical step for rigorous validation of both simulation and experimental results. This insufficient (or inadequate) model checking also reveals, on the

other hand, that physical models lack proper scrutiny about their simplifying assumptions and thus about their reliability (see, for example, §§A.5). As a result of this, it seems that certain detailed multiscale models can behave as much as “black box” models, despite of their apparent mathematical complexity (e.g., as it is the case of some articles that have been published on recent years, which applied the Lattice-Boltzmann-Method in structure-resolved simulations of SOFC porous layers). Thus, from this perspective, to skip model checking amounts to bringing about illusory conclusions, which raise confusion and controversial perceptions on the apparent success of these models.

Hopefully, the issues discussed in this work should open up a perspective towards needed improvements in the direction of more consistent (and reliable) mathematical models, including comprehensive and rigorous comparison between simulations and experimental data, a praxis that is presently missing for the type of problems that have been addressed herein. When building the necessary models, future developments should offer a theoretical assessment of multicomponent mass transfer in the so-called idealized “capillary pore spaces”, which are used as an abstraction for the pore-level information in phenomenological models. Through a concerted description of what (supposedly) occurs at the pore level, one expects that it will make apparent the flagrant oversimplifications (*i.e.*, misrepresentations of transport processes) made by several SOFC models, permitting a more accurate picture of cell macroscale performance. Due to the aforementioned limitations placed by (possibly) not considering physically relevant phenomena in the numerical simulation of SOFCs, it would be of great interest to study the following topics in future research projects:

- I. Discuss important issues related to equation physical scaling, when “matching” macroscale-continuum and pore-level mesoscale descriptions (*i.e.*, coarse-graining of subgrid-scale processes in governing equations and closure relations). For instance, the effect of mass density variations over distances comparable to pore dimensions in the development of macroscale models.
- II. Provide a better presentation material and discussion about the “transport regime” referred to as hydrodynamic diffusion, clearly differentiating the concepts/definitions of self-diffusion, transport diffusion, and mutual diffusion.
- III. Provide a better presentation material and discussion about the Knudsen “diffusion”, including the importance of the non-maxwellian behavior of fluid particles under the effect of surface roughness (pore-wall fractal scaling) within the SOFC porous space (*i.e.*, “anomalous Knudsen diffusion”). Moreover, discuss the possible influence of Knudsen layer on surface reaction rates (see item “X” below).

- IV. Properly incorporate the diffusion slip (Kramers-Kistemaker effect) mechanism into the modeling framework and discuss its (qualitative and quantitative) importance on simulation results (for both porous medium and gas channel domains).
- V. Verify the consistency (e.g., mass conservativity) of mixture-averaged rules and rigorous multicomponent theories on the calculation of diffusion fluxes and transport properties (e.g., diffusivities and viscosities) in porous medium systems.
- VI. Discuss Fickian formalism considering the presence of wall-effects, chemical reactions, and local force fields, aiming at a more physically consistent description of non-fickian behaviors (e.g., “corrected Maxwell-Stefan formalism”). Ideally, this discussion should include a comparative analysis of multicomponent diffusion according to: (i) TIP; (ii) extended non-equilibrium theories; and (iii) kinetic theories.
- VII. Discuss the “real” significance of convection for transport processes in porous membranes, based on the derivation of more rigorous (e.g., extended hydrodynamics) macroscopic transport equations for multicomponent rarefied gas flows (i.e., “flow in the near-continuum regime”). Discussions about the hypothesis of interpenetrating fluid-continua and fluid mixture theories should be considered.
- VIII. Provide a better presentation material and discussion about transport coefficients in the case of coupled transport mechanisms and consequent cross-effects (e.g., chemical viscosity, barodiffusion, shear-induced migration, and so forth).
- IX. Discuss other important issues related to macroscale-continuum models, such as: (i) the inclusion of spurious mass sources in balance equations during the derivation of Jaumann’s entropy equation and its relation to the correct definition of mass diffusion fluxes (in terms of an unambiguous frame of reference) in different types of mechanically constrained porous membranes; (ii) consistent flux-matching boundary conditions for chemical reactions on porous-walls (see item “XI”); (iii) the scale invariance of entropy production (“extremal entropy principles”) and how to perform consistent coarse-graining of subgrid-scale processes when deriving macroscale models.
- X. Discuss the significance of the Lattice-Boltzmann equation (and thus of the Lattice-Boltzmann method) to, in fact, describe phenomena beyond hydrodynamics in SOFCs, including a more encompassing analysis of its application to multicomponent flows in the transition regime (e.g., the so-called multiple-relaxation-time Lattice-Boltzmann methods for micro-flows).
- XI. Discuss the characterization of simultaneous fluid transport and chemical reaction in multiscale porous media, including key aspects such as: (i) the correct definition (and use) of lumped parameters (e.g., the role of tortuosity) in upscaled macroscale-continuum models (i.e., in models based on the so-called “effective medium theory”); (ii) how to properly account for the presence of adsorption fields

on pore-scale through an upscaled, continuum formulation of reaction-transport equations; (iii) the pertinence of considering the so-called “Brickman correction” in Darcy’s law-based constitutive equations, as a way to consistently account for the “upscaled effect” of chemical reactions near (or on) the “dead-end” walls of porous channels (thus, in this case, also considering a discussion about the correct prescription of macroscopic boundary conditions in the presence of heterogeneous reactions that results in non-zero Stefan velocities); (iv) the scale (microstructure-related) dependence of apparent (upscaled) electrochemical reaction rates and their influence on the evaluation of the effective diffusivity of gas components in porous media; (v) and, more generally, the upscaling of reaction-transport process in porous media with fast and finite-rate kinetics, and the potential failure of macroscale-continuum models under the conditions of (subgrid) mixing-controlled heterogeneous reactions.

- XII. After the above items have been properly addressed and then incorporated into a more encompassing mathematical model, one should try to evaluate to what extent mass transfer limitations can indeed impact design decisions and thus the cost evaluation of SOFC devices.

APPENDIX A

PROOFS AND DERIVATIONS

A.1	Solution for the Governing Equation in §§3.3.2.....	(pg. 209)
A.2	Derivation and Discussion of Kulikovsky's Analytical Models.....	(pg. 211)
A.3	On the Apparent Inconsistency of η_{conc} in Kim <i>et al.</i> (1999).....	(pg. 222)
A.4	Axial Momentum Equation (Gas Channel) in Janardhanan <i>et al.</i> (2007).....	(pg. 225)
A.5	A Reasoning for the “Average Bosanquet Formula” (Ternary Gas Mixture).....	(pg. 226)

Appendix A

PROOFS AND DERIVATIONS

A.1. Solution for the Governing Equation in §§3.3.2

Equation (3.48) is a nonhomogeneous, 2nd order ODE that can be analytically solved by traditional methods, such as “the method of undetermined coefficients”, subjected to the following boundary conditions:

$$\Theta_{O_{ad}^{2-}} \Big|_{y=0} = \Theta_{O_{ad}^{2-}}^{TPB} \quad (A.1)$$

$$\frac{\partial \Theta_{O_{ad}^{2-}}}{\partial y} \Big|_{y=L_s} = 0 \quad (A.2)$$

The Newman-type boundary condition, Eq. (A.2), represents a no-flux condition at the plane $y = L_s$, according to Fig. 3.5. The Dirichlet-type boundary condition, Eq. (A.1), represents the relationship between the surface potential step ($\Delta\phi_s$) and surface coverage perturbation at the TPB. In order to calculate $\Theta_{O_{ad}^{2-}}^{TPB}$ one may apply, for instance, either Eq. (3.38) or (3.40). Thus, if one assumes the condition of low surface coverage, then

$$\Theta_{O_{ad}^{2-}}^{TPB} = \sqrt{p_{O_2,tpb}} K_{O_s^{2-}} \exp \left[-\frac{2\mathcal{F}}{\mathcal{R}T} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \right] \quad (A.3)$$

The solution of Eq. (3.48) has the following general form:

$$\Theta_{O_{ad}^{2-}}(y) = C_1 \exp \left(\sqrt{K_{O_s^{2-}} \sqrt{p_{O_2}}/Y^2} y \right) + C_2 \exp \left(-\sqrt{K_{O_s^{2-}} \sqrt{p_{O_2}}/Y^2} y \right) + K_{O_s^{2-}} \sqrt{p_{O_2}} \quad (A.4)$$

where C_1 and C_2 are integration constants to be determined. By applying Eq. (A.2) to (A.4) one obtains

$$C_1/C_2 = \exp \left(-2L_s \sqrt{K_{O_s^{2-}} \sqrt{p_{O_2}}/Y^2} \right) \quad (A.5)$$

Then, substituting Eq. (A.1) and (A.3) in Eq. (A.4) leads to

$$\Theta_{O_{ad}^{2-}}^{TPB} = \mathcal{C}_1 + \mathcal{C}_2 + K_{O_s^{2-}} \sqrt{p_{O_2}} = K_{O_s^{2-}} \sqrt{p_{O_2}} \exp \left[-\frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \right] \quad (A.6)$$

Expanding the exponential term on the RHS of Eq. (A.6) in a Taylor series up to the first order (and still assuming that $\Theta_{O_{ad}^{2-}}^{TPB} \ll 1$), then

$$\begin{aligned} \mathcal{C}_1 + \mathcal{C}_2 + K_{O_s^{2-}} \sqrt{p_{O_2}} &= K_{O_s^{2-}} \sqrt{p_{O_2}} \left[1 - \frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \right] \\ \Rightarrow \mathcal{C}_1 + \mathcal{C}_2 &= -K_{O_s^{2-}} \sqrt{p_{O_2}} \frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \end{aligned} \quad (A.7)$$

Thus from Eq. (A.5) and (A.7),

$$\begin{aligned} \mathcal{C}_2 &= -K_{O_s^{2-}} \sqrt{p_{O_2}} \frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \left[1 + \exp \left(-2L_s \sqrt{K_{O_s^{2-}} \sqrt{p_{O_2}} / Y^2} \right) \right]^{-1} \\ \mathcal{C}_1 &= -K_{O_s^{2-}} \sqrt{p_{O_2}} \frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \left[1 + \exp \left(2L_s \sqrt{K_{O_s^{2-}} \sqrt{p_{O_2}} / Y^2} \right) \right]^{-1} \end{aligned} \quad (A.8)$$

The solution of Eq. (3.48) can now be expressed as

$$\Theta_{O_{ad}^{2-}}(y) = K_{O_s^{2-}} \sqrt{p_{O_2}} \left[1 - \frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \frac{\cosh \left(y \sqrt{\frac{1}{Y_*^2}} \right) + \cosh \left((2L_s - y) \sqrt{\frac{1}{Y_*^2}} \right)}{1 + \cosh \left(2L_s \sqrt{\frac{1}{Y_*^2}} \right)} \right] \quad (A.9)$$

where the term Y_*^2 is given by Eq. (3.52). The RHS of Eq. (A.9) may be further simplified as follows:

$$1 + \cosh(2L_s \sqrt{1/Y_*^2}) = 2 \cosh^2 \left(L_s \sqrt{1/Y_*^2} \right) \quad (A.10)$$

$$\begin{aligned} &\cosh(y \sqrt{1/Y_*^2}) + \cosh((2L_s - y) \sqrt{1/Y_*^2}) = \\ &= \cosh(y \sqrt{1/Y_*^2}) + \cosh(2L_s \sqrt{1/Y_*^2}) \cosh(-y \sqrt{1/Y_*^2}) + \sinh(2L_s \sqrt{1/Y_*^2}) \sinh(-y \sqrt{1/Y_*^2}) \\ &= \cosh(y \sqrt{1/Y_*^2}) + \left[2 \cosh^2(L_s \sqrt{1/Y_*^2}) - 1 \right] \cosh(-y \sqrt{1/Y_*^2}) + \\ &\quad + 2 \sinh(L_s \sqrt{1/Y_*^2}) \cosh(L_s \sqrt{1/Y_*^2}) \sinh(-y \sqrt{1/Y_*^2}) \\ &= 2 \cosh(L_s \sqrt{1/Y_*^2}) \left[\sinh(L_s \sqrt{1/Y_*^2}) \sinh(-y \sqrt{1/Y_*^2}) + \cosh(L_s \sqrt{1/Y_*^2}) \cosh(-y \sqrt{1/Y_*^2}) \right] \\ &= 2 \cosh(L_s \sqrt{1/Y_*^2}) \cosh[(L_s - y) \sqrt{1/Y_*^2}] \end{aligned} \quad (A.11)$$

Substituting Eq. (A.10) and (A.11) in Eq. (A.9) finally yields

$$\Theta_{O_{ad}^{2-}}(y) = K_{O_s^{2-}} \sqrt{p_{O_2}} \left[1 - \frac{2\mathcal{F}}{\mathcal{RT}} \Theta_{O_{ad}^{2-}}^{TPB} (\Delta\phi_s)_{max} \frac{\cosh \left((L_s - y) \sqrt{\frac{1}{Y_*^2}} \right)}{\cosh \left(L_s \sqrt{\frac{1}{Y_*^2}} \right)} \right] \quad (A.12)$$

A.2. Derivation and Discussion of Kulikovsky's Analytical Models

The starting point is the base model as proposed by Kulikovsky^[12], which describes the processes shown on Fig. 2.10. Here this model is first presented in its original form (with respect to the definition given to “ η ” by that author), and then modifications and the reasoning for such modifications are discussed. In §§2.3.3 and §§2.3.4 it was brought to light a number of questions concerning the reaction penetration depth parameter and the meaning of “ η ”. At this point some of Kulikovsky's implied assumptions are pinpointed and the conceptual “imprecisions” of his model revealed. Analytical models are derived for the particular cases of ideal ionic transport and ideal gas-phase transport, and for each of these cases the limiting situations of high and low current density are considered for further simplifications. Kulikovsky^[12, 107] starts with the following system of equations, which governs the active layer performance:

$$\frac{\partial i_{io}(z)}{\partial z} = -i_F^{\vee}(z) = -i_*^{\vee} (C/C_{ref})^a \left[\exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(\frac{(1-\alpha) F \eta}{RT}\right) \right] \quad (\text{A.13})$$

$$i_{io} = -\sigma_{io} \frac{\partial \eta(z)}{\partial z} \quad (\text{A.14})$$

$$D \frac{\partial C(z)}{\partial z} = \frac{i - i_{io}}{z_e F} \quad (\text{A.15})$$

where z is the coordinate along the active layer thickness (note that on Figure 2.10 it is directed from the electrolyte to the anode out layer); $i_*^{\vee}$ is the volumetric exchange current density; C_{ref} is a reference molar concentration of feed gas; a is the reaction order in respect to feed gas; η is the half-cell (e.g., anodic) overvoltage; σ_{io} is the effective conductivity of electrolyte phase in the active layer; D is the effective diffusion coefficient of feed gas within the porous channels of the active layer; and α is a charge transfer coefficient.

According to Kulikovsky, Eq. (A.13) expresses the decay of ionic current with z at a rate given by Butler–Volmer electrode kinetics (RHS of this equation); Eq. (A.14) states that Ohm's law is valid for the electrolyte phase, relating the ionic current to the overvoltage gradient; Eq. (A.15) is a material balance that establishes¹ that the local diffusion flux of feed gas is equal to the local electronic current density ($i_e = i - i_{io}$) to be converted through the half-cell electrochemical reaction (molar flux of ions to be converted into free electrons); and the stoichiometry factor $z_e F$ in Eq. (A.15) does the conversion of current density to molar flux.

¹ Kulikovsky did not mention, but it is also implied that the electrolyte boundary is impermeable to feed gas in order to derive Eq. (A.15).

The RHS of Eq. (A.13) can be further simplified. The first exponential describes the forward electrochemical conversion (e.g., hydrogen oxidation reaction) while the second exponential represents the reverse reaction. This reverse reaction lowers the overall rate of conversion in near equilibrium situations ($\eta \cong 0$), when both exponentials in Eq. (A.13) are of the same order of magnitude. Now, If one assumes that the active layer operates far from equilibrium (i.e., $\eta \gtrsim \alpha \mathcal{F}/(\mathcal{R}T)$), then the second exponential may be ignored. Or, alternatively and in order to simplify the calculations, the transfer coefficient may be adopted² as $\alpha = 1 - \alpha = 0.5$. The latter option will be used herein. It is worth while noting that, under the Butler–Volmer formalism, the constraint $\alpha = 0.5$ is important within the region of small current densities, wherein both exponentials contributes to the activation polarization. At larger currents (SOFC “operating far from equilibrium”), however, the second exponential is negligible and hence the value of α in Eq. (A.13) is of minor importance, even though it should still be consistent (that is, its value is not arbitrary, as asserted by some authors in the literature). Equation (A.13) can now be rewritten as:

$$\frac{\partial i_{io}(z)}{\partial z} = -i_*^{\mathbb{V}} (C/C_{ref})^a [\exp(\eta/b_{ts}) - \exp(-\eta/b_{ts})] = -2 i_*^{\mathbb{V}} (C/C_{ref})^a \sinh(\eta/b_{ts}) \quad (\text{A.16})$$

Where

$$b_{ts} = \frac{\mathcal{R} T}{\alpha \mathcal{F}} \quad (\text{A.17})$$

is the Tafel slope. To nondimensionalize Eq. (A.14), (A.15), and (A.16), the following dimensionless variables are introduced:

$$\hat{z} = \frac{z}{l_t}, \quad \hat{\eta} = \frac{\eta}{b_{ts}}, \quad \hat{C} = \frac{C}{C_t}, \quad \hat{i}_{io} = \frac{i_{io} l_t}{\sigma_{io} b_{ts}} \quad (\text{A.18})$$

where C_t is the feed gas concentration at the active layer/outlet layer interface (at $z/l_t = 1$, according to Fig. 2.10). Note that hereafter the subscripts “0” and “t” will mark the values at $\hat{z} = 0$ and $\hat{z} = 1$, respectively. With these variables, equations are now written as

$$\epsilon^2 \frac{d\hat{i}_{io}}{d\hat{z}} = -(\hat{C}/\hat{C}_{ref})^a \sinh \hat{\eta} \quad (\text{A.19})$$

$$\hat{i}_{io} = -\frac{d\hat{\eta}}{d\hat{z}} \quad (\text{A.20})$$

$$\hat{D} \frac{d\hat{C}}{d\hat{z}} = \hat{i} - \hat{i}_{io} \quad (\text{A.21})$$

Where

² There are also physical justifications on why this is a good approximation under certain (realistic) operating conditions^[8, 67].

$$\epsilon = \sqrt{\frac{\sigma_{io} b_{ts}}{2 i_*^{\vee} l_t^2}} = \frac{l_N}{l_t} \quad (\text{A.22})$$

is the dimensionless Newman's reaction penetration depth or RPD^[67]. This parameter indicates, under ideal transport conditions of gas species, how deep the reaction penetrates into the electrode (see §§2.3.3). In dimensional form it is expressed as

$$l_N = \sqrt{\sigma_{io} b_{ts} / (2 i_*^{\vee})} \quad (\text{A.23})$$

The dimensionless effective diffusion coefficient of feed gas is given by

$$\hat{D} = \frac{z_e \mathcal{F} D C_t}{\sigma_{io} b_{ts}} \quad (\text{A.24})$$

Boundary conditions for the system (A.19)-(A.21) are

$$\hat{i}_{io}(\hat{z} = 0) = \hat{i} = \frac{i l_t}{\sigma_{io} b_{ts}}, \quad \hat{i}_{io}(\hat{z} = 1) = 0 \quad (\text{A.25})$$

$$\hat{C}(\hat{z} = 1) = 1 \quad (\text{A.26})$$

The system of equations (A.19)-(A.21), which is controlled by three main parameters (ϵ , $\hat{D}$, and $\hat{i}$), describes the spatial distribution of state variables (ionic current, overvoltage, gas concentration, and the rate of electrochemical reaction) in the active layer. From the point of view of SOFC electrochemical performance, the polarization curve of the active layer, expressed through the relation $\hat{\eta}_0 = \hat{\eta}_0(\hat{i})$, is what constitutes the main goal of the cell modeling when it is applied to describe the cell behavior in response to various values of ϵ and $\hat{D}$. The “total” voltage loss (polarization) is given by the value of η_0 at the active layer/electrolyte interface. The shape of the reaction rate, $i_F^{\vee}(z)$, is also relevant in that it might support the optimization of catalyst design (e.g., load distribution in terms of g cat./cm²) within the electrode. Even though analytical solution for the system (A.19)-(A.21) is as yet unknown, for the two limiting cases of (i) ideal ionic transport or (ii) ideal gas-phase transport explicit analytical solutions can be derived.

A.2.1 Ideal Ionic Transport (Diffusion-Limited Case)

In the case of ideal ionic transport, Kulikovsky assumes that the overvoltage gradient is vanishing small ($\nabla \hat{\eta} \rightarrow 0$) and thus that, in the system (A.19)-(A.21), the approximation $\hat{\eta} \cong \hat{\eta}_0$ is valid (in §§2.3.4 it was shown that this assumption is not consistent at all). Consequentially, in this simplified model Eq. (A.20) is disregarded. The following system results:

$$\epsilon^2 \frac{d\hat{i}_{io}}{d\hat{z}} = -(\hat{C}/\hat{C}_{ref})^a \sinh \hat{\eta}_0 \quad (\text{A.27})$$

$$\hat{D} \frac{d\hat{C}}{d\hat{z}} = \hat{i} - \hat{i}_{io} \quad (\text{A.28})$$

It is also assumed that the electrochemical reaction is of first-order with respect to feed gas ($\alpha = 1$). Differentiating Eq. (A.27) with respect to $\hat{z}$ and substituting the term $d\hat{C}/d\hat{z}$ in Eq. (A.28) yields

$$\frac{d^2 \hat{i}_{io}}{d\hat{z}^2} = -\zeta^2 (\hat{i} - \hat{i}_{io}), \quad \hat{i}_{io}(0) = \hat{i}, \quad \hat{i}_{io}(1) = 0 \quad (\text{A.29})$$

where the characteristic length ζ is

$$\zeta = \sqrt{\frac{\sinh \hat{\eta}_0}{\epsilon^2 \hat{C}_{ref} \hat{D}}} \quad (\text{A.30})$$

The solution of Eq. (A.29) is^[12]

$$\hat{i}_{io}(\hat{z}) = \hat{i} \left(1 - \frac{\sinh(\zeta \hat{z})}{\sinh \zeta} \right) \quad (\text{A.31})$$

And then solving Eq. (A.27) for $\hat{C}$, the solution is^[12]

$$\hat{C}(\hat{z}) = -\left(\frac{\epsilon^2 \hat{C}_{ref}}{\sinh \hat{\eta}_0} \right) \frac{d\hat{i}_{io}}{d\hat{z}} = -\frac{1}{\hat{D} \zeta^2} \frac{d\hat{i}_{io}}{d\hat{z}} \quad (\text{A.32})$$

After differentiating Eq. (A.31) and substituting it in the result above, one has

$$\hat{C}(\hat{z}) = \frac{\hat{i} \cosh(\zeta \hat{z})}{\hat{D} \zeta \sinh \zeta} \quad (\text{A.33})$$

For the dimensionless rate of electrochemical oxidation one finds that:

$$\begin{aligned} \hat{R}_{OR}(\hat{z}) &= -\frac{d\hat{i}_{io}}{d\hat{z}} = \frac{\hat{i} \zeta \cosh(\zeta \hat{z})}{\sinh \zeta} \\ \Rightarrow \hat{R}_{OR}(\hat{z}) &= \hat{D} \zeta^2 \hat{C}(\hat{z}) \end{aligned} \quad (\text{A.34})$$

It is readily seen that, in the case of ideal ionic transport, the shape of $\hat{R}_{OR}(\hat{z})$ closely follows that of $\hat{C}(\hat{z})$, as depicted in Fig. A-1. When the gas diffusivity is relatively small (*i.e.*, large ζ) electrochemical conversion occurs within a small region near the active layer/outer layer interface, in which the reacting gas is, still, in excess (see Fig. A-1). Kulikovsky proposes a characteristic length for this region, defined as:

$$\hat{l}_N = \frac{1}{\zeta} = \epsilon \sqrt{\frac{\hat{D} \hat{C}_{ref}}{\sinh \hat{\eta}_0}} \quad (\text{A.35})$$

Nonetheless, that author does not indicate the considerations used to obtain this relation. It is only mentioned that the quantity $\hat{l}_N$ follows from Eq. (A.34), considering that this equation dictates the rate of decay of $\hat{R}_{OR}(\hat{z})$. Most likely, Kulikovsky developed the following rationale:

$$\Delta \hat{l}_N = \hat{l}_N(\hat{z}) - \hat{l}_N(0) = \left(\frac{d\hat{R}_{OR}}{d\hat{z}} \right)^{-1} (\hat{R}_{OR}(\hat{z}) - \hat{R}_{OR}(0)) = \frac{1}{\zeta \tanh(\zeta \hat{z})} \quad (\text{A.36})$$

$$\text{for } \zeta \gg 1 \text{ and } \hat{z} = 1 \Rightarrow \tanh(\zeta \hat{z}) \simeq 1 \quad \therefore \hat{l}_N = \Delta \hat{l}_N \simeq \frac{1}{\zeta}$$

Thus we see that this characteristic length, for the case of ideal ionic transport, is not generally valid and it is applicable only for large values of ζ (see also Eq. (A.45)). Finally, the polarization curve of the active layer can be obtained by setting $\hat{z} = 1$ (thus $\hat{C} = 1$) in Eq. (A.33):

$$\hat{i} = \hat{D} \zeta \tanh \zeta, \quad \text{where } \zeta = \zeta(\hat{\eta}_0) \quad (\text{A.37})$$

Figure A-1: diffusion-limited case (large $\zeta \cong 10$): profiles of ionic current density $\hat{i}_{io}$, feed gas concentration $\hat{C}$, overvoltage $\hat{\eta}$, and rate of electrochemical conversion $\hat{R}_{OR}$ within the active layer. Parameters used: $\hat{\eta}_0 = 3.0$; $\hat{D} = 0.1$; $\epsilon = 1$; $\hat{i} = 1$; $\hat{C}_{ref} = 1$.

In the particular case of Fig. A-1, the corresponding value of $\hat{l}_N$ is $\cong 0.1$, when this is evaluated using Eq. (A.35). However, by inspecting Fig. A-1 one verifies that this value does not seem to be consistent at all: instead, one should have that $\hat{l}_N \cong 0.4 - 0.5$. The likely reason for such discrepancy is because Eq. (A.35) is an asymptotic result; whereas the modeling equations applied by Kulikovskiy had not assumed this asymptotic limit in their derivations. Simulations indicate, for the situation depicted in Fig. A-1, the necessity of $\zeta \gtrsim 100$ in order to Eq. (A.35) provide reasonable values. Alternatively, a better way to estimate $\hat{l}_N$ would be to define some objective criterion for the decay of $\hat{R}_{OR}$. For instance, $\hat{l}_N$ may be defined as the length above which the rate $\hat{R}_{OR}$ falls below 1% of its initial value (at $\hat{z} = 1$). Thus, in this case, one finds that $\hat{l}_N \cong 0.46$. For this kind of definition, the following alternative expression could be utilized:

$$\begin{aligned} \hat{R}_{OR}(\hat{z} = 1 - \hat{l}_N) / \hat{R}_{OR}(\hat{z} = 1) &= \cosh(\zeta(1 - \hat{l}_N)) / \cosh(\zeta) \cong 0.01 \\ \Rightarrow 1 - \hat{l}_N &\cong \frac{\operatorname{arcosh}(0.01 \cosh \zeta)}{\zeta} \end{aligned} \quad (\text{A.38})$$

A.2.1.1 Low Cell Current ($\zeta \ll 1$)

In the low current regime, $\tanh \zeta \simeq \zeta$ and Eq. (A.37) reduces to $\hat{i} = \hat{D} \zeta^2$. Using Eq. (A.30) the polarization curve is now given by

$$\hat{\eta}_0 = \arcsin(\hat{C}_{ref} \epsilon^2 \hat{i}) \quad (\text{A.39})$$

Note that $\hat{D}$ does not appear in this relation. In this case, a small ζ implies that η_0 is also small or, alternatively, that the diffusion coefficient is large (assuming that electrode kinetics is the same in both cases). Thus, the gas transport does not contribute to the voltage loss in this limiting case. Using Eq. (A.39) and Eq. (A.35), the characteristic thickness of the reacting region is

$$\hat{l}_N = \sqrt{\hat{D}/\hat{i}} \quad \text{or in dimensional form,} \quad l_N = \sqrt{z_e \mathcal{F} C_t l_t / i} \quad (\text{A.40})$$

Therefore, the validity of the low-current approximation may be conditionally expressed as:

$$\zeta \ll 1 \Rightarrow \sqrt{\hat{D}/\hat{i}} \gg 1 \Rightarrow \hat{l}_N \gg 1 \quad (\text{A.41})$$

A.2.1.2 High Cell Current ($\zeta \gg 1$)

In the high current regime, $\tanh \zeta \cong 1$ and Eq. (A.37) reduces to $\hat{i} = \hat{D} \zeta$. Using Eq. (A.30) the polarization curve is now given by

$$\hat{\eta}_0 = \arcsin(\hat{C}_{ref} \epsilon^2 \hat{i}^2 / \hat{D}) \quad (\text{A.42})$$

Additionally, if $\epsilon / \sqrt{\hat{D}} \gtrsim 1$ then the argument of archsin in Eq. (A.42) is large and thus one may apply the approximation $\arcsin y \simeq \ln 2y$. In this case,

$$\hat{\eta}_0 = 2 \ln \left(\epsilon \hat{i} \sqrt{2 \hat{C}_{ref} / \hat{D}} \right) \quad \text{or in dimensional form,} \quad \eta_0 = 2 b_{ts} \ln(i / i_{crit,D}) \quad (\text{A.43})$$

Equation (A.43) exhibits the so-called double (or doubled) Tafel slope. The term $i_{crit,D}$ is a characteristic current threshold value, called “critical current density”, defined as:

$$i_{crit,D} = \sqrt{i_*^{\mathbb{V}} z_e \mathcal{F} D C_t^2 / C_{ref}} \quad (\text{A.44})$$

Using Eq. (A.42) and Eq. (A.35), the characteristic thickness of the reacting region is calculated as

$$\hat{l}_N = \hat{D} / \hat{i} \quad \text{or in dimensional form,} \quad l_N = z_e \mathcal{F} C_t D / i \quad (\text{A.45})$$

Therefore, the validity of the high-current approximation may be conditionally expressed as:

$$\zeta \gg 1 \Rightarrow \sinh \hat{\eta}_0 \gg \epsilon^2 \hat{C}_{ref} \hat{D} \Rightarrow \hat{i} \gg \hat{D} \quad (\text{A.46})$$

A.2.2 Ideal Gas Transport (Ionic Conduction-Limited Case)

For the case of ideal gas transport, Kulikovsky^[12,107] assumes that the feed gas concentration gradient is vanishing small ($\nabla \hat{C} \rightarrow 0$) and thus that, without loss of generality, one could set $\hat{C} = \hat{C}_{ref} = 1$ and disregard Eq. (A.21). The following simplified system would result:

$$\epsilon^2 \frac{d\hat{i}_{io}}{d\hat{z}} = -\sinh \hat{\eta} \quad (\text{A.47})$$

$$\hat{i}_{io} = -\frac{d\hat{\eta}}{d\hat{z}} \quad (\text{A.48})$$

And the boundary conditions for this system are also given by Eq. (A.25). Differentiating Eq. (A.47) with respect to $\hat{z}$, using Eq. (A.48), and knowing that hyperbolic sine and cosine satisfy the known identity $\cosh^2(\hat{\eta}) - \sinh^2(\hat{\eta}) = 1$, one obtains:

$$\begin{aligned} \epsilon^2 \frac{d^2 \hat{i}_{io}}{d\hat{z}^2} &= -\cosh \hat{\eta} \frac{d\hat{\eta}}{d\hat{z}} = \hat{i}_{io} \cosh \hat{\eta} \\ \epsilon^2 \frac{d^2 \hat{i}_{io}}{d\hat{z}^2} &= \hat{i}_{io} \sqrt{1 + \sinh^2(\hat{\eta})} = \hat{i}_{io} \sqrt{1 + \left(-\epsilon^2 \frac{d\hat{i}_{io}}{d\hat{z}}\right)^2} = \hat{i}_{io} \sqrt{1 + \epsilon^4 \left(\frac{d\hat{i}_{io}}{d\hat{z}}\right)^2} \\ \therefore \epsilon^2 \frac{d^2 \hat{i}_{io}}{d\hat{z}^2} &= \hat{i}_{io} \sqrt{1 + \epsilon^4 \left(\frac{d\hat{i}_{io}}{d\hat{z}}\right)^2} \end{aligned} \quad (\text{A.49})$$

In the limiting cases of (i) small and (ii) large current densities, Eq. (A.49) can be analytically solved.

A.2.2.1 Low Cell Current

In order to solve Eq. (A.49) in the low current limit, Kulikovsky neglected the term multiplying $d\hat{i}_{io}/d\hat{z}$ altogether. However, although in this case the current density $\hat{i}$ is assumed to be small, the current gradient might not be so (e.g., if the active layer happens to be very thin). Moreover, the fourth power of the term ϵ could be comparatively large as well (see Eq. (A.22)):

$$\epsilon^4 \left(\frac{d\hat{i}_{io}}{d\hat{z}}\right)^2 \propto \left(\frac{\sigma_{io} b_{ts}}{2 i_*^\vee l_t^2} \frac{\delta i_{io}}{\delta z} \frac{l_t/(\sigma_{io} b_{ts})}{1/l_t}\right)^2 \propto \left(\frac{\delta i_{io}}{\delta z}\right)^2 \frac{1}{(2 i_*^\vee)^2} \propto \left(\frac{i}{l_t}\right)^2 \frac{1}{(2 i_*^\vee)^2} \quad (\text{A.50})$$

The product $\epsilon^4 d\hat{i}_{io}/d\hat{z}$ scales with the square of i/l_t . Thus, even though i is small, in the case when the layer is very thin their combined effect might not be negligible. Thus, one verifies that

the condition of low current is not enough to discard $d\hat{i}_{io}/d\hat{z}$ on the RHS of Eq. (A.49). A condition such as:

$$\frac{i}{l_t} \ll 2 i_*^{\mathbb{V}} \quad \text{or,} \quad \frac{i}{2 i_*^{\mathbb{V}}} \ll l_t \quad \text{or still,} \quad \frac{i}{2 l_t i_*^{\mathbb{V}}} \ll 1 \quad (\text{A.51})$$

would be required³. All in all, neglecting $\epsilon^4 d\hat{i}_{io}/d\hat{z}$ from Eq. (A.49) gives:

$$\epsilon^2 \frac{d^2 \hat{i}_{io}}{d\hat{z}^2} = \hat{i}_{io} \quad , \quad \hat{i}_{io}(\hat{z} = 0) = \hat{i} \quad , \quad \hat{i}_{io}(\hat{z} = 1) = 0 \quad (\text{A.52})$$

which is integrated to yield

$$\hat{i}_{io}(\hat{z}) = \frac{\hat{i} \sinh[(1 - \hat{z})/\epsilon]}{\sinh(1/\epsilon)} \quad (\text{A.53})$$

The profile of $\hat{\eta}$ follows from Eq. (A.47):

$$\hat{\eta}(\hat{z}) = \arcsin \left[\frac{\epsilon \hat{i} \cosh((1 - \hat{z})/\epsilon)}{\sinh(1/\epsilon)} \right] \quad (\text{A.54})$$

And for the reaction rate $\hat{R}_{OR} = -d\hat{i}_{io}/d\hat{z}$

$$\hat{R}_{OR}(\hat{z}) = \frac{\hat{i} \cosh[(1 - \hat{z})/\epsilon]}{\epsilon \sinh(1/\epsilon)} \quad (\text{A.55})$$

In this case of low cell current densities, the characteristic scale of all profiles is given by Newman's RPD ϵ . Meaning that, for large ϵ , the characteristic length scale of $\hat{R}_{OR}$ and $\hat{\eta}$ greatly exceeds the active layer thickness (see Fig. A-2). On the other hand, small ϵ means high exchange current density ($i_*^{\mathbb{V}}$), which makes possible to convert the ionic current close to the electrolyte without significant voltage loss. Thus, for small ϵ there is a rapid decay in the profiles of $\hat{i}_{io}$, $\hat{R}_{OR}$, and $\hat{\eta}$ (see the top plot in Fig. A-2).

³ Alternatively, Kulikovskiy^[12] has also provided a validity condition in the low-current limit, expressed by the inequality $\epsilon \hat{i} < \coth(1/\epsilon)$.

Figure A-2: ionic conduction-limited case (in the low-current limit): profiles of the ionic current density $\hat{i}_{io}$, overvoltage $\hat{\eta}$, and rate of electrochemical conversion $\hat{R}_{OR}$ in the active layer. Parameters used: $\hat{i} = 0.1$; (a) $\epsilon = 0.1$; and (b) $\epsilon = 10$.

Setting $\hat{z} = 0$ in Eq. (A.54) we obtain the polarization curve of the active layer:

$$\hat{\eta}_0 = \arcsin[\epsilon \hat{i} \coth(1/\epsilon)] \quad (\text{A.56})$$

when $\epsilon \ll 1$, then $\coth(1/\epsilon) \simeq 1$ and Eq. (A.56) reduces to

$$\hat{\eta}_0 = \arcsin(\epsilon \hat{i}), \quad \epsilon \ll 1 \quad (\text{A.57})$$

when $\epsilon \gg 1$, then $\coth(1/\epsilon) \simeq \epsilon$ and Eq. (A.56) reduces to

$$\hat{\eta}_0 = \arcsin(\epsilon^2 \hat{i}), \quad \epsilon \gg 1 \quad (\text{A.58})$$

This last case occurs when both the gas transport and ionic transport are admitted ideal. Additionally, if $\epsilon^2 \hat{i} \geq 2$ the arcsin may be replaced by the logarithm of double argument, and so

$$\hat{\eta}_0 = \ln(2 \epsilon^2 \hat{i}), \quad \epsilon \gg 1, \quad \epsilon^2 \hat{i} \geq 2 \quad (\text{A.59})$$

which in dimensional form is

$$\eta_0 = b_{ts} \ln \left[\frac{i}{i_*^\vee l_t C_t / C_{ref}} \right] \quad (\text{A.60})$$

The result of Eq. (A.60), widely applied in the literature, is thus based on the assumptions of Tafel kinetics, uniform reaction rate distribution, and on a moderated-to-low exchange current density.

A.2.2.2 High Cell Current

In order to solve Eq. (A.49) in the high current limit, Kulikovsky^[12] neglected the first term on the RHS. Thus (note that as $d\hat{i}_{io}/d\hat{z} < 0$ and the function is monotonic, the negative value of the square root is considered)

$$\frac{d^2 \hat{i}_{io}}{d\hat{z}^2} = -\hat{i}_{io} \frac{d\hat{i}_{io}}{d\hat{z}}, \quad \hat{i}_{io}(\hat{z} = 0) = \hat{i}, \quad \hat{i}_{io}(\hat{z} = 1) = 0 \quad (\text{A.61})$$

or

$$2 \frac{d^2 \hat{i}_{io}}{d\hat{z}^2} + \frac{d(\hat{i}_{io}^2)}{d\hat{z}} = 0 \quad (\text{A.62})$$

which is partially integrated to yield

$$2 \frac{d \hat{i}_{io}}{d\hat{z}} + \hat{i}_{io}^2 = -(-2\hat{R}_{OR}(0) - \hat{i}^2) = -2\hat{R}_{OR}(1) \quad (\text{A.63})$$

The solution to Eq. (A.63) is^[12]

$$\hat{i}_{io}(\hat{z}) = \beta_0 \tan[\beta_0(1 - \hat{z})/2] \quad (\text{A.64})$$

where

$$\beta_0 = \sqrt{2\hat{R}_{OR}(0) - \hat{i}^2} \quad (\text{A.65})$$

The profile of $\hat{\eta}$ follows from Eq. (A.47) and Eq. (A.64):

$$\hat{\eta}(\hat{z}) = \arcsin \left\{ \frac{\beta_0^2 \epsilon^2}{2} [1 + \tan^2(\beta_0(1 - \hat{z})/2)] \right\} \quad (\text{A.66})$$

and for the reaction rate $\hat{R}_{OR} = -d\hat{i}_{io}/d\hat{z}$

$$\hat{R}_{OR}(\hat{z}) = \frac{\beta_0^2}{2} [1 + \tan^2(\beta_0(1 - \hat{z})/2)] \quad (\text{A.67})$$

In order to avoid iterative calculation of β_0 , an approximate expression may be developed. Setting $\hat{z} = 0$ in Eq. (A.64)

$$\hat{i}_{io}(\hat{z} = 0) = \hat{i} = \beta_0 \tan[\beta_0/2] \quad (\text{A.68})$$

Because $\hat{i}$ is large (e.g., $\hat{i} > 15$), $\beta_0 \rightarrow \pi \Rightarrow \tan(\beta_0/2) \simeq 2/(\pi - \beta_0)$. Using this result in Eq. (A.68) and solving for β_0 , one obtains

$$\beta_0 \simeq \hat{i} \pi / (2 + \hat{i}) \Leftrightarrow \hat{i} = 2\beta_0 / (\pi - \beta_0) \quad (\text{A.69})$$

One verifies that the profiles of $\hat{i}(\hat{z})$ and $\hat{R}_{OR}(\hat{z})$ do not depend on ϵ and they contain only one parameter, β_0 , which is itself function only of $\hat{i}$. Thus in the high current limit these profiles do not depend on Newman's RPD. In place of that, the characteristic thickness decreases with the growth of the cell current $\hat{i}$. It can be shown that^[109]

$$\hat{l}_N \simeq \frac{1}{\hat{i}} \quad \text{or in dimensional form,} \quad l_N \simeq \frac{\sigma_{io} b_{ts}}{i} \quad (\text{A.70})$$

Therefore, the dominating factor in the limit of high current densities is the poor ionic transport, regardless of the exchange current density. In this case, most of the electrochemical conversion takes place close to the electrolyte, where the losses associated with ion transport are lower (see Fig. A-3). A simplified polarization curve for this case was also derived as^[107]:

$$\hat{\eta}_0 = 2 \ln(\epsilon \hat{i}) \quad (\text{A.71})$$

which in dimensional form is

$$\eta_0 = 2 b_{ts} \ln(i/i_{crit,\sigma}) \quad (\text{A.72})$$

where the “characteristic critical current density” $i_{crit,\sigma}$ is

$$i_{crit,\sigma} = \sqrt{2 i_*^\vee \sigma_{io} b_{ts} (C_t/C_{ref})} \quad (\text{A.73})$$

Figure A-3: ionic conduction-limited case (high-current limit): profiles of the ionic current density $\hat{i}_{io}$, overvoltage $\hat{\eta}$, and the rate of electrochemical conversion $\hat{R}_{OR}$ within the active layer. Parameters used were: $\epsilon = 1.0$; (a) $\beta_0 = 2.7$; and (b) $\beta_0 = 3.0$.

Equation (A.72) exhibits a doubled Tafel slope, indicating that when there is poor ionic conductivity the electrochemical conversion “is forced” to occur close to the electrolyte interface (in order to minimize ohmic losses). Thus, in this case there is a consequent shift of the on-set overvoltage, *i.e.* a change of the value $\eta(z = 0)$. Kulikovsky^[12] did also provide a condition for the validity of the high-current approximation, expressed by the inequality $\epsilon \hat{t} > 4 \coth(1/\epsilon)$.

A.3. On the Apparent Inconsistency of η_{conc} in Kim *et al.* (1999)

Apparently, there is an inconsistency in “Eq. [26]” of Kim *et al.*^[82], pp 73. The anodic and cathodic concentration polarization terms were not divided by the partial pressure of the hydrogen from the fuel stream (outside of the anode) and by the partial pressure of the oxygen from the oxidant stream, (outside of the cathode), respectively. The issue appears to be related to the definition of concentration polarization. They have stated with their “Eq. [26]” that (here neglecting the ohmic and activation polarizations, so to simplify the discussion)

$$E_{\text{cell}}(i) = E^{\text{th}} - \eta_{\text{conc,an}}^*(i) - |\eta_{\text{conc,ca}}^*(i)| \quad (\text{A.74})$$

However, it should have been expressed as

$$E_{\text{cell}}(i) = E_{\text{rev}}^{\text{bulk}} - \eta_{\text{conc,an}}(i) - |\eta_{\text{conc,ca}}(i)| \quad (\text{A.75})$$

Considering that when $i = 0$, E_{cell} corresponds to the open-circuit limit, *i.e.*

$$E_{\text{cell}}(i = 0) = E_{\text{rev}}^{\text{bulk}} = E^{\text{th}} + \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{\text{H}_2}^{\text{bulk}} a_{\text{O}_2}^{\text{bulk}^{1/2}}}{a_{\text{H}_2\text{O}}^{\text{bulk}}} \right) \quad (\text{A.76})$$

Then from Eq. (3.7), (3.12), and (A.76)

$$\begin{aligned} E^{\text{th}} - \eta_{\text{conc,an}}^* - |\eta_{\text{conc,ca}}^*| &= E_{\text{rev}}^{\text{bulk}} - \eta_{\text{conc,an}} - |\eta_{\text{conc,ca}}| \\ -\eta_{\text{conc,an}}^* - |\eta_{\text{conc,ca}}^*| &= \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{\text{H}_2}^{\text{bulk}} a_{\text{O}_2}^{\text{bulk}^{1/2}}}{a_{\text{H}_2\text{O}}^{\text{bulk}}} \right) - \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{\text{H}_2}^{\text{bulk}} a_{\text{H}_2\text{O}}^{\text{tpb}}}{a_{\text{H}_2\text{O}}^{\text{bulk}} a_{\text{H}_2}^{\text{tpb}}} \right) - \frac{\mathcal{R}T}{4\mathcal{F}} \ln \left(\frac{a_{\text{O}_2}^{\text{bulk}}}{a_{\text{O}_2}^{\text{tpb}}} \right) \end{aligned} \quad (\text{A.77})$$

From Kim *et al.*^[82], the concentration polarization was defined as (pp. 73):

$$\eta_{\text{conc,an}}^* = -\frac{\mathcal{R}T}{2\mathcal{F}} \ln(p_{\text{H}_2}^{\text{bulk}} - f_{\text{an}} i) + \frac{\mathcal{R}T}{2\mathcal{F}} \ln(p_{\text{H}_2\text{O}}^{\text{bulk}} + f_{\text{an}} i) = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{p_{\text{H}_2\text{O}}^{\text{tpb}}}{p_{\text{H}_2}^{\text{tpb}}} \right) \quad (\text{A.78})$$

$$|\eta_{\text{conc,ca}}^*| = -\frac{\mathcal{R}T}{4\mathcal{F}} \ln \left[p_{\text{O}_2}^{\text{bulk}} - \left(\frac{p - p_{\text{O}_2}^{\text{bulk}}}{p} \right) f_{\text{ca}} i \right] = \frac{\mathcal{R}T}{4\mathcal{F}} \ln \left(\frac{1}{p_{\text{O}_2}^{\text{tpb}}} \right) \quad (\text{A.79})$$

After substituting Eq. (A.78) and (A.79) in Eq. (A.77), one has that (also assuming $p = p_{\text{th}}$)

$$-\frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{p_{\text{H}_2\text{O}}^{\text{tpb}}}{p_{\text{H}_2}^{\text{tpb}}} \right) - \frac{\mathcal{R}T}{4\mathcal{F}} \ln \left(\frac{1}{p_{\text{O}_2}^{\text{tpb}}} \right) \equiv -\frac{\mathcal{R}T}{2\mathcal{F}} \ln \left(\frac{a_{\text{H}_2\text{O}}^{\text{tpb}}}{a_{\text{H}_2}^{\text{tpb}}} \right) - \frac{\mathcal{R}T}{4\mathcal{F}} \ln \left(\frac{1}{a_{\text{O}_2}^{\text{tpb}}} \right) \quad (\text{A.80})$$

which leaves one with a consistent result in this regard. Thus, one sees that Kim and coauthors indeed have applied a different definition of concentration polarization in their “Eq. [26]”, when compared to that of Eq. (3.7) and (3.12). The difference is

$$\begin{aligned}\Delta\eta_{conc,an}^* &= \eta_{conc,an} - \eta_{conc,an}^* = \frac{\mathcal{R}T}{2\mathcal{F}} \ln(a_{H_2}^{bulk}/a_{H_2O}^{bulk}) \\ \Delta\eta_{conc,ca}^* &= |\eta_{conc,ca}| - |\eta_{conc,ca}^*| = \frac{\mathcal{R}T}{4\mathcal{F}} \ln(a_{O_2}^{bulk})\end{aligned} \quad \therefore \Delta\eta_{conc}^* = E_{rev}^{bulk} \quad (A.81)$$

Therefore, Kim *et al.* in [82] “discounts” the value of the cell reversible voltage (E_{rev}^{bulk}) from the concentration polarization. Such peculiar choice of definition seems, though possible, quite strange. Moreover, the argument inside the exponential is, based on their definition, Eq. (A.79), not dimensionless, thereby constituting a physical inconsistency (even though it is mathematically acceptable). For that it is often recommended to use the chemical activity (or fugacity coefficients at the chosen reference pressure) until substitution of dimensional values in the final result. Either way, the definition proposed by Kim *et al.*^[82], according to Eq. (A.78) and (A.79), is conceptually incompatible when compared to the definition of concentration polarization as established by Eq. (3.7) and (3.12). Nevertheless, at the end of their paper the authors have changed the definition of η_{conc} , more precisely in their “Eq. 36” and “Eq. 45”, but they have not included any reasoning for such change.

A.4. Axial Momentum Equation in Janardhanan *et al.* (2007)

Equation (4.47a) (*i.e.*, axial momentum balance within the gas channel) can be written in a more general form as:

$$\frac{\partial(\rho u)}{\partial t} + \text{div}(\rho \vec{V} u) = \rho \left[\frac{\partial u}{\partial t} + \vec{V} \cdot \text{grad}(u) \right] + u \left[\frac{\partial \rho}{\partial t} + \text{div}(\rho \vec{V}) \right] \quad (\text{A.82})$$

Equation (4.47a) is identical to Eq. (A.82) if and only if the first term on the RHS of Eq. (A.82) is identically zero, so that the continuity equation is verified:

$$\text{s. t. } u \left[\frac{\partial \rho}{\partial t} + \text{div}(\rho \vec{V}) \right] = u \frac{P_e}{\mathcal{A}_c} \left[\sum_k M_k \tilde{N}_k \right] \quad (\text{A.83})$$

Then,

$$\rho \left[\frac{\partial u}{\partial t} + \vec{V} \cdot \text{grad}(u) \right] = 0 \Leftrightarrow \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = 0 \quad (\text{A.84})$$

In other words, the above result represents a tacit imposition in that the substantial (or material) derivative is zero,

$$\rho \frac{Du}{Dt} \equiv \rho \left[\frac{\partial u}{\partial t} + \vec{V} \cdot \text{grad}(u) \right] = 0 \quad (\text{A.85})$$

One can also express Eq. (A.85) as:

$$\rho \frac{Du}{Dt} \equiv \frac{\partial(-p + \tau_{v,xx})}{\partial x} + \frac{\partial \tau_{v,yx}}{\partial y} + \frac{\partial \tau_{v,zx}}{\partial z} + \dot{S}_{Mx} = 0 \quad (\text{A.86})$$

Therefore, the implied assumption is that both the pressure gradient and shear stress change are either zero, negligible small, or that they balance (cancel) each other out. Moreover, any eventual source term $\dot{S}_{Mx}$ must be also either zero, negligible small, or it must balance the other remaining parcels of Eq. (A.86). From Eq. (A.84), in the steady-state, one also has that

$$u \frac{\partial u}{\partial x} = 0 \quad (\text{A.87})$$

Thus $u(x) = \text{const.}, \forall x$. In this case the axial velocity is constant throughout the gas channel and thus solving an additional momentum equation would not be necessary⁴ (*e.g.*, u is completely defined by specifying the inflow mass flux). Therefore, the axial momentum equation in Janardhanan *et al.*^[298] is really an artifact introduced by the under-relaxation procedure used for the numerical solution of the system of equations.

⁴ Note that if the mean gas composition varies in the (mean) flow direction, the viscosity μ may also vary axially along the channel length. Therefore, in the general case, the mean wall shear stress may also not be constant throughout the channel.

A.5. A Reasoning for the “Average Bosanquet Formula”

The “extended version” of Bosanquet formula provided in Table 4.15^[313], when compared to its classical form^[62], is an artifice a few authors in the literature have been using as a “non-rigorous” method to avoid the violation of gas species mass conservation. Although the conditions under which it should be applied, its apparent validity, and its mathematical derivation has not been openly discussed (e.g., see [72, 313]), it is most likely that the use of an “averaged Bosanquet diffusion coefficient” is justified in the cases where the assumption of constant total pressure is incorrectly enforced in the presence of chemical reactions (which, in this case, produce a net change in the total number density of gas species). Below it is given a possible explanation for the origin for such “corrected formula” for the case of a ternary gas mixture.

The simpler EPDM model of Virkar and coauthors (see §§ 4.4.2) will be employed in this attempt of explanation, starting from Eq. (4.15a), (4.15b), and (4.18), which at this point assume that the microstructure of porous electrodes is not a function of position and thus that D_{an}^{eff} is composition-independent. As the saturation current is also a function of the hydrogen concentration at bulk conditions, it is convenient to define an effective anodic transport multiplier (ψ_{an}) as:

$$\psi_{an} = \frac{\delta_{an}}{D_{an}^{eff}} = \left(\frac{\tau_{an}^2 \delta_{an}}{D_{an} \varepsilon_{an}} \right)_{eff} = \int_0^{\delta_{an}} \frac{\tau_{an}^2(z)}{D_{an}(z) \varepsilon_{an}(z)} dz \quad (A.88)$$

with

$$D_{an}^{eff} = \frac{D_{an} \varepsilon_{an}}{\tau_{an}^2} = \frac{\delta_{an}}{[\tau_{an}^2 \delta_{an} / (D_{an} \varepsilon_{an})]_{eff}} \quad (A.89)$$

The factor ψ_{an} is akin to that of Virkar^[82], with the exception that in this case the diffusion coefficient is also admitted to be a function of position (*i.e.*, D_{an} is not composition-independent and thus it might also vary along the layer thickness). It is an approximate average based on the “mean value” of $\tau_{an}^2 / (D_{an} \varepsilon_{an})$ in the interval $[0, \delta_{an}]$. By assuming only diffusive mass transport mechanism, from Eq. (4.14), (4.41), and (A.88) one may express the limiting molar flux as

$$\tilde{N}_{H_2,lim} = \frac{i_{as}}{2F} = \frac{p_{H_2}^{bulk}}{RT \psi_{an}} = (\psi_{an})^{-1} C_{H_2}^{bulk} \quad (A.90)$$

The factor ψ_{an} may be seen as the reciprocal of an “effective mass transfer coefficient” in the very special situation (or rather, assumption) in which the interfacial partial pressure of hydrogen reaches zero at current saturation condition (*i.e.*, zero gas concentration at the

anode/electrolyte interface). If one now defines $\psi_{an}^* = \psi_{an} RT/(2F)$, Eq. (A.88) and (A.89) can be rewritten as:

$$p_{H_2}^{a/e} = p_{H_2}^{bulk} - \psi_{an}^* i_F \quad (A.91)$$

$$p_{H_2O}^{a/e} = p_{H_2O}^{bulk} + \psi_{an}^* i_F \quad (A.92)$$

For a ternary gas system under approximately constant total pressure (**there is an error in this assumption**), the composition profile of an inert gas (e.g., Ar, N₂, CO₂) may be calculated as^[82]:

$$-\frac{p}{RT} \frac{dy_{inert}}{dz} = \frac{\tilde{N}_{inert}}{D_{inert}^{Kn}} + \frac{y_{H_2} \tilde{N}_{inert} - y_{inert} \tilde{N}_{H_2}}{(\varepsilon_{an}/\tau_{an}^2) \mathfrak{D}_{inert,H_2}} + \frac{y_{H_2O} \tilde{N}_{inert} - y_{inert} \tilde{N}_{H_2O}}{(\varepsilon_{an}/\tau_{an}^2) \mathfrak{D}_{inert,H_2O}} \quad (A.93)$$

Because the net flow of the inert gas is zero ($\tilde{N}_{inert} = 0$) and $\tilde{N}_{H_2} = -\tilde{N}_{H_2O}$ in steady state (**another common misleading assumption made in the literature**), Eq. (A.93) becomes

$$-\frac{p}{RT} \frac{dy_{inert}}{dz} = \frac{\tilde{N}_{H_2}}{(\varepsilon_{an}/\tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2O}} - \frac{1}{\mathfrak{D}_{inert,H_2}} \right) y_{inert} \quad (A.94)$$

Integration of Eq. (A.94) gives

$$y_{inert}^{a/e} = y_{inert}^{bulk} \exp \left[\frac{RT \tilde{N}_{H_2} \delta_{an}}{p (\varepsilon_{an}/\tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2}} - \frac{1}{\mathfrak{D}_{inert,H_2O}} \right) \right] \quad (A.95)$$

Or yet as a function of the position along layer thickness,

$$y_{inert}(z) = y_{inert}^{bulk} \exp \left[\frac{RT \tilde{N}_{H_2}}{p (\varepsilon_{an}/\tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2}} - \frac{1}{\mathfrak{D}_{inert,H_2O}} \right) z \right] \quad (A.96)$$

Thus y_{inert} varies exponentially as a function of position and this variation along the electrode may not be (aprioristically) assumed to be negligible small (insignificant). Therefore, this aspect should be taken into consideration in the evaluation of H_2 diffusion coefficient when it is not independent of position. Similarly to the case of inert gas in Eq. (A.94), one can write for H_2

$$-\frac{p}{RT} \frac{dy_{H_2}}{dz} = \frac{\tilde{N}_{H_2}}{(\varepsilon_{an}/\tau_{an}^2)} \left(\frac{1}{D_{H_2}^{Kn}} + \frac{y_{inert}(z)}{\mathfrak{D}_{H_2,inert}} + \frac{1 - y_{inert}(z)}{\mathfrak{D}_{H_2,H_2O}} \right) \quad (A.97)$$

Or, alternatively, in a similar form to Fick's Law:

$$\tilde{N}_{H_2} = -\frac{p}{RT} \frac{\varepsilon_{an}}{\tau_{an}^2} D_{H_2} \frac{dy_{H_2}}{dz} \quad (A.98)$$

where D_{H_2} can be defined as the H_2 “bulk” multicomponent diffusion coefficient for the ternary system $H_2 - H_2O - Inert$ (in the absence of a porous body), and expressed as:

$$D_{H_2} = \left(\frac{1}{D_{H_2}^{Kn}} + \frac{y_{inert}(z)}{\mathfrak{D}_{H_2,inert}} + \frac{1 - y_{inert}(z)}{\mathfrak{D}_{H_2,H_2O}} \right)^{-1} \quad (A.99)$$

Now using the result of Eq. (A.88) one can write

$$D_{H_2}^{\text{eff}} = \frac{\delta_{an}}{\psi_{an}} = \frac{\varepsilon_{an}}{\tau_{an}^2} \left(\frac{1}{\delta_{an}} \int_0^{\delta_{an}} \frac{1}{D_{H_2}(z)} dz \right)^{-1} \cong \frac{\varepsilon_{an}}{\tau_{an}^2} \left(\frac{1}{D_{H_2}^{Kn}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2,inert}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} \right)^{-1} \quad (\text{A.100})$$

And $\bar{y}_{inert}$ is evaluated as

$$\bar{y}_{inert} = \frac{y_{inert}^{\text{bulk}}}{\delta_{an}} \int_0^{\delta_{an}} \exp \left[\frac{\mathcal{R}T \tilde{N}_{H_2}}{p(\varepsilon_{an}/\tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2}} - \frac{1}{\mathfrak{D}_{inert,H_2O}} \right) z \right] dz \quad (\text{A.101})$$

$$\bar{y}_{inert} = \frac{y_{inert}^{\text{bulk}}}{\delta_{an} \Upsilon} [\exp(\delta_{an} \Upsilon) - 1] \quad \text{with} \quad \Upsilon = \frac{i_F \mathcal{R}T}{2\mathcal{F} p(\varepsilon_{an}/\tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2}} - \frac{1}{\mathfrak{D}_{inert,H_2O}} \right) \quad (\text{A.102})$$

Where the boundary condition Eq. (4.14) has been substituted in $\tilde{N}_{H_2}$. The integration parameter Υ (m^{-1}) may be understood as the reciprocal of a mass transport penetration depth, that is, the dimensionless quantity $\delta_{an} \Upsilon$ indicates “how deep the inert gas concentration profile penetrates into the electrode”. In Eq. (A.91) and (A.92) the factor ψ_{an}^* is calculated using Eq. (A.100):

However, unfortunately, Eq. (4.15) and (4.16) from the work of Virkar^[82] (and thus, as a consequence, Eq. (A.91) and (A.92)) must be corrected (“normalized”) for the limiting case when $i_F = i_{as}$ and $p_{H_2}^{a/e} = 0$. Otherwise, mole fractions will not sum to one! That is, one must have $p_{inert}^{a/e} = p - p_{H_2O}^{a/e}$. Virkar and coauthors have neglected this aspect in [259] and made a mistake because they did not use the correct effective diffusion coefficient in the H_2O mass balance. Thus, their equivalent to equation Eq. (4.16) is in error and violates mass conservation. Moreover, Eq. (4.25) is also incorrect and must be fixed!

$$1 - y_{H_2O}^{a/e} = y_{inert}^{a/e} \quad (\text{A.103})$$

$$p_{H_2O}(z=0, i_F = i_{as}) = p_{H_2O}^{a/e} = p_{H_2O}^{\text{bulk}} + \frac{\mathcal{R}T \tau_{an}^2 \delta_{an}}{2\mathcal{F} D_{H_2O} \varepsilon_{an}} i_{as} \quad (\text{A.104})$$

$$\begin{aligned}
1 - \left(y_{H_2O}^{bulk} + \frac{\mathcal{R} T \tau_{an}^2 \delta_{an}}{2\mathcal{F} p D_{H_2O} \varepsilon_{an}} i_{as} \right) &= y_{inert}^{a/e} \\
y_{H_2}^{bulk} + y_{inert}^{bulk} - \frac{\mathcal{R} T \tau_{an}^2 \delta_{an} i_{as}}{2\mathcal{F} p \varepsilon_{an}} \left(\frac{1}{D_{H_2O}^{Kn}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2O,inert}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} \right) &= y_{inert}^{a/e} \\
\frac{\mathcal{R} T \tau_{an}^2 \delta_{an}}{2\mathcal{F} p D_{H_2}^{eff} \varepsilon_{an}} i_{as} - \frac{\mathcal{R} T \tau_{an}^2 \delta_{an} i_{as}}{2\mathcal{F} p \varepsilon_{an}} \left(\frac{1}{D_{H_2O}^{Kn}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2O,inert}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} \right) &= y_{inert}^{a/e} - y_{inert}^{bulk} \\
\frac{\mathcal{R} T \tau_{an}^2 \delta_{an} i_{as}}{2\mathcal{F} p \varepsilon_{an}} \left[\frac{1}{D_{H_2}^{Kn}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2,inert}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} - \left(\frac{1}{D_{H_2O}^{Kn}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2O,inert}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} \right) \right] &= y_{inert}^{a/e} - y_{inert}^{bulk} \\
\frac{\mathcal{R} T \tau_{an}^2 \delta_{an} i_{as}}{2\mathcal{F} p \varepsilon_{an}} \left[\frac{1}{D_{H_2}^{Kn}} - \frac{1}{D_{H_2O}^{Kn}} + \bar{y}_{inert} \left(\frac{1}{\mathfrak{D}_{H_2,inert}} - \frac{1}{\mathfrak{D}_{H_2O,inert}} \right) \right] &= y_{inert}^{a/e} - y_{inert}^{bulk}
\end{aligned} \tag{A.105}$$

$$\begin{aligned}
\frac{\mathcal{R} T \tau_{an}^2 \delta_{an} i_{as}}{2\mathcal{F} p \varepsilon_{an}} \left[\frac{y_{inert}^{bulk}}{\delta_{an} \Upsilon} [\exp(\delta_{an} \Upsilon) - 1] \left(\frac{1}{\mathfrak{D}_{H_2,inert}} - \frac{1}{\mathfrak{D}_{H_2O,inert}} \right) \right] &= y_{inert}^{a/e} - y_{inert}^{bulk} \\
y_{inert}^{bulk} [\exp(\delta_{an} \Upsilon) - 1] &= y_{inert}^{a/e} - y_{inert}^{bulk} \\
[\exp(\delta_{an} \Upsilon) - 1] &= y_{inert}^{a/e} / y_{inert}^{bulk} - 1 \\
\delta_{an} \Upsilon &= \ln(y_{inert}^{a/e}) - \ln(y_{inert}^{bulk})
\end{aligned}$$

The result above is consistent with Eq. (A.96) and (A.102) if and only if one assumes $D_{H_2}^{Kn} = D_{H_2O}^{Kn}$! This a direct (**and obviously incorrect**) result of assuming that the total pressure is constant (*i.e.*, $\nabla p = 0$) in the derivation of Eq. (A.93). Thus, based on Eq. (A.95)

$$\begin{aligned}
y_{inert}^{a/e} &= y_{inert}^{bulk} \exp \left[\frac{\mathcal{R} T \tilde{N}_{H_2} \delta_{an}}{p (\varepsilon_{an} / \tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2}} - \frac{1}{\mathfrak{D}_{inert,H_2O}} \right) \right] \\
\Leftrightarrow \ln(y_{inert}^{a/e}) - \ln(y_{inert}^{bulk}) &= \frac{\mathcal{R} T \tilde{N}_{H_2} \delta_{an}}{p (\varepsilon_{an} / \tau_{an}^2)} \left(\frac{1}{\mathfrak{D}_{inert,H_2}} - \frac{1}{\mathfrak{D}_{inert,H_2O}} \right) \\
\Leftrightarrow \ln(y_{inert}^{a/e}) - \ln(y_{inert}^{bulk}) &= \delta_{an} \Upsilon
\end{aligned} \tag{A.106}$$

One sees that both the LHS and RHS of Eq. (A.105) are in fact equal. In this case, therefore, “corrected” expressions for the EPDM should be written as:

$$i_{as} = \frac{2\mathcal{F} p_{H_2}^{bulk} D_{H_2}^{eff}}{\mathcal{R} T \delta_{an}} \tag{A.107}$$

$$p_{H_2}(z=0) = p_{H_2}^{a/e} = p_{H_2}^{bulk} - \frac{\mathcal{R} T \tau_{an}^2 \delta_{an}}{2\mathcal{F} D_{H_2}^* \varepsilon_{an}} i_F \Rightarrow p_{H_2}^{a/e} = p_{H_2}^{bulk} \left(1 - \frac{i_F}{i_{as}} \right) \tag{A.108}$$

$$p_{H_2O}(z=0) = p_{H_2O}^{a/e} = p_{H_2O}^{bulk} + \frac{\mathcal{R} T \tau_{an}^2 \delta_{an}}{2\mathcal{F} D_{H_2O}^* \varepsilon_{an}} i_F \Rightarrow p_{H_2O}^{a/e} = p_{H_2O}^{bulk} \left(1 + \frac{i_F p_{H_2}^{bulk}}{i_{as} p_{H_2O}^{bulk}} \frac{D_{H_2}^{eff,*}}{D_{H_2O}^{eff,*}} \right) \quad (A.109)$$

with effective diffusion coefficients now expressed as

$$\frac{D_{H_2}^{eff,*}}{D_{H_2O}^{eff,*}} = \left(\frac{1}{D_{an}^{avr}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2O,inert}} \right) \left(\frac{1}{D_{an}^{avr}} + \frac{\bar{y}_{inert}}{\mathfrak{D}_{H_2,inert}} \right)^{-1} \quad (A.110)$$

Where

$$D_{an}^{avr} = \frac{1}{2} \left[\left(\frac{1}{D_{H_2O}^{Kn}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} \right)^{-1} + \left(\frac{1}{D_{H_2}^{Kn}} + \frac{1 - \bar{y}_{inert}}{\mathfrak{D}_{H_2,H_2O}} \right)^{-1} \right] \quad (A.111)$$

Equation (A.110) represents some form of an “averaged Bosanquet formula”, similar to that given by Eq. (4.54b) in Table 4.15. This equation “artificially” satisfies the condition of mass conservation when substituted in Eq. (A.105).

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