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Estudos de eletrocatalisadores baseados em Pt, Mo e W como ânodos tolerantes ao CO em célula a combustível de membrana trocadora de prótons (PEMFC)

Studies of Pt, Mo and W based electrocatalysts as CO tolerant anodes in proton exchange membrane fuel cell (PEMFC)

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Definiteness of purpose is
the starting point of all
achievements.

W. Clement Stone

DEDICATION

I dedicate this thesis to
my family.

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Abstract

Enhanced CO tolerance and stability are necessary requirements for the proper performance of anodic electrocatalysts of proton exchange membrane fuel cell (PEMFC) operating with reformat fuel. In this work carbon and carbides (molybdenum and tungsten carbides) supported electrocatalysts have been studied for the activity of hydrogen oxidation reaction (HOR), CO tolerance and stability in the anode of a PEMFC. The materials investigated include: PtMo/C, PtMo/C heat-treated, Pt/Mo₂C/C, PtMo/Mo₂C/C, PtW/C, Pt/WC/C and Pt/C. Differences in electrocatalysts morphology were characterized by temperature programmed reduction (TPR), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM) and wavelength dispersive spectroscopy (WDS). The electrochemical characteristics and activity of electrocatalysts were evaluated for the HOR and CO tolerance by single cell polarization measurements and cyclic voltammetry in the form of gas diffusion electrodes. Online mass spectrometry (OLMS) and CO stripping experiments were performed to evaluate the CO tolerance mechanism of the electrocatalysts. Cyclic voltammetry up to 5000 potential cycles was conducted to evaluate the electrocatalyst stability. It was observed that the carbon supported PtMo heat-treated at 600 °C with average crystallite size of 16.7 nm and Pt supported on Mo₂C/C showed an enhanced stability and a good hydrogen electrooxidation activity in the presence of 100 ppm CO, as compared to as prepared carbon supported PtMo and molybdenum carbide supported PtMo electrocatalysts. Similarly, better CO tolerance and stability were shown by tungsten carbide supported Pt electrocatalyst, as compared to carbon supported PtW electrocatalyst. Cyclic voltammetry and WDS results showed that partial dissolution of Mo and W and their migration/diffusion from the anode towards cathode take place during the cycling process, which was the major cause of performance losses of these electrocatalysts. On the basis of polarization measurements and cyclic voltammograms of both anodes and cathodes, it was concluded that the stability of these electrocatalysts may be improved either by heat-treatment or the formation of carbides in their supports.

Keywords: Catalysts, stability, CO tolerance, fuel cell, PtMo/C catalyst.

Resumo

Elevada tolerância ao CO e alta estabilidade são requisitos necessários para o desempenho apropriado de eletrocatalisador anódico de células a combustível de membrana protônica (PEMFC) operando com combustível reformado. Neste trabalho eletrocatalisadores suportados em carbono e carbetos (carbetos de molibdênio e tungstênio) foram estudados para a reação de oxidação de hidrogênio (ROH), tolerância ao CO e estabilidade no ânodo de uma PEMFC. Os materiais investigados incluem: PtMo/C, PtMo/C tratado-termicamente, Pt/Mo₂C/C, PtMo/Mo₂C/C, PtW/C, Pt/WC/C e Pt/C. As diferenças na morfologia dos eletrocatalisadores foram caracterizadas por redução com temperatura programada (TPR), difração de raios-x (XRD), microscopia eletrônica de transmissão (MET), energia dispersiva de raios-x (EDX), espectroscopia de absorção de raios-X (XAS), microscopia eletrônica de varredura (MEV) e espectroscopia de dispersão de comprimento de onda (WDS). As características e as atividades eletroquímicas dos electrocatalisadores foram avaliadas para ROH e tolerância ao CO por medidas de curvas de polarização e voltametria cíclica em célula unitária, sob a forma de eletrodos de difusão de gás. Experimentos de espectrometria de massa (EMS) “on-line” e de stripping de CO foram realizados para avaliar o mecanismo de tolerância ao CO dos eletrocatalisadores. Voltametria cíclica conduzida até 5000 ciclos foi realizada para avaliar a estabilidade dos eletrocatalisadores. Observe-se que os eletrocatalisadores de PtMo suportado em carbono e tratado a 600°C, com tamanho médio de cristalito de 16,7 nm, e de Pt suportado em Mo₂C mostraram uma estabilidade melhorada e boa atividade para a eletroxidação de hidrogênio na presença de 100 ppm de CO, em comparação com os catalisadores de PtMo suportado em carbono e PtMo suportado em carbeto de molibdênio. Similarmente, melhores tolerância ao CO e estabilidade foram mostradas para o eletrocatalisador de Pt suportado em carbeto de tungstênio, quando comparado ao de PtW suportado em carbono. Os resultados de voltametria cíclica e WDS mostraram que ocorre dissolução parcial de Mo e W e sua migração/difusão do ânodo para o cátodo durante o processo de ciclagem, o que foi a maior causa das perdas em desempenho destes eletrocatalisadores. Baseado nas medidas de polarização e nos voltamogramas cíclicos de ambos ânodos e cátodos, concluiu-se que a estabilidade destes eletrocatalisadores pode ser melhorada seja por tratamento térmico ou pela formação de carbetos nos seus suportes.

Palavras chaves: Catalisadores, estabilidade, tolerância ao CO, célula a combustível, catalisador de PtMo/C.

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List of Abbreviations

PEMFC – Proton exchange membrane fuel cell

HOR – Hydrogen oxidation reaction

TPR – Temperature programmed reduction

XRD – X-ray diffraction

TEM – Transmission electron microscopy

EDS – Energy dispersive spectroscopy

XAS – X-ray absorption spectroscopy

XANES – X-ray absorption near edge structure

SEM – Scanning electron microscopy

WDS – Wavelength dispersive spectroscopy

OLMS – Online mass spectrometry

FCT – Fuel cell technology

PAFC – Phosphoric acid fuel cell

AFC – Alkaline fuel cell

MCFC – Molten carbonate fuel cell

DMFC – Direct methanol fuel cell

CL – Catalyst layer

GDL – Gas diffusion layer

MEA – Membrane electrode assembly

PTFE – Polytetrafluoroethylene

ORR – Oxygen reduction reaction

WGSR – Water gas shift reaction

PGMs – Platinum group metals

DoE – Department of energy

GC – Gas chromatography

PFSA – Perfluorosulfonic acid

TCD – Thermal conductivity detector

TPC – Thin porous coating

BLNNano – Brazilian Nano Technology National Laboratory

CNPEM – Centro Nacional de Pesquisa em Energia e Materiais

EXAFS – Extended X-ray absorption fine structure

BLNLS – Brazilian Synchrotron National Light Laboratory

BSE – Back scattered electron

SE – Secondary electron

EMR – Electromagnetic radiation

FE-SEM – Field emission scan electron microscopy

EPMA – Electron probe microanalysis

FAMAF – Faculty of Mathematics, Astronomy and Physics

AST – Accelerated stress test

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CHAPTER I

INTRODUCTION

1. INTRODUCTION

The development of fuel cell has received great attention since the end of the nineteenth century. In the middle of the twentieth century fuel cell technology (FCT) became more general and global when more serious ecological problems such as global warming and greenhouse effect in cities were recognized. FCT is also being proposed to move from non-renewable natural sources such as fossils fuels towards renewable sources such as hydroelectric and solar power.

1.1. What is a fuel cell

More precisely, fuel cell is an electrochemical device designed to convert the chemical energy of a reaction directly into electrical energy. The difference between the fuel cell and battery is that, the maximum energy provided by a battery is determined by the amount of chemical reactant stored within it. The battery will no longer produce electrical energy, when the limiting reactants are consumed. On the other hand, fuel cell is an electrochemical device that theoretically has the capability of producing electrical energy for as long as the fuel and oxidant are supplied to the electrodes.

1.2. Brief history of fuel cell

Fuel cells were first developed in 1839 by Sir William Robert Groove, a judge and an amateur natural scientist [1]. He conducted a series of experiment on water electrolysis in a device, which he called gas voltaic battery. This device consisted of two platinum electrodes immersed into sulfuric acid solution. While doing water electrolysis, he presumed that if water can be decomposed to H_2 and O_2 by the passage of electric current, there should be possibility for the opposite reaction to take place. In 1932, Frances Thomas Bacon, a British

professor in the Cambridge University, worked on developing the alkaline fuel cell, which was called Bacon cell. This cell was capable of producing a power of 5 to 6 kW. However, due to high gas pressure (20 to 40 bar) used, the cell was very heavy [2]. In 1960, the Bacon patent was licensed to the aircraft and engine manufacturer Pratt and Whitney. Their aim was to lower the pressure inside the cell by using a very high alkali concentration. These P & W fuel cells were used for the Apollo spacecraft. Later on, the fuel cell developed by Thomas Grubb and Leonard Niedrich (1960s) was used for power generation in the Gemini spacecraft [2]. There have since been many efforts done on the development of various types of fuel cells and today several power plants which are based on fuel cell have been manufactured and operated successfully with the capacity ranging from several kilowatts to tens of megawatts.

1.3. Working principle of fuel cell

A fuel cell consists of an electrolyte layer sandwiched between two porous electrodes. The basic principle of fuel cell is illustrated in Figure 1 [3]. In a typical fuel cell, H_2 fuel is continuously fed to the anode and O_2 or air is continuously fed to the cathode. Electric current is produced as a result of electrochemical reactions taking place at the electrodes. The electrons produced flow through the external circuit, which can be utilized for electrical power applications. The function of porous electrodes is two-fold; 1) they offer a higher true working surface area 2) they provide the sites, where the reactions occurs along the three-phase boundaries between the solid catalyst, the gaseous reactant and the electrolyte. A uniform distribution of reaction sites is in favor of the efficient operation of the porous electrodes.

1.4. Types of fuel cells

Based on the type of electrolyte used, there are various types of fuel cells that are made from different materials and operate on different fuels. They can be classified as: 1) proton exchange membrane fuel cell (PEMFC); 2) phosphoric acid fuel cell (PAFC); 3)

alkaline fuel cell (AFC); 4) molten carbonate fuel cell (MCFC) and 5) solid oxide fuel cell (SOFC) [1,4,5]. An exception to this classification is the direct methanol fuel cell (DMFC) which is a fuel cell where the methanol is directly fed to the anode. The electrolyte of this cell is not determining for the class.

In proton exchange membrane or polymer electrolyte fuel cell the electrolyte consists of a polymeric proton exchange membrane (fluorinated sulfonic acid polymer or other similar polymer), which promotes the conduction of protons. In the presence of water, this membrane serves as an excellent proton conductor, because when it swells, it leads to the dissociation of acidic functional groups and formation of free protons. Water management is of critical importance in the operation of PEM fuel cell. Since the membrane needs to remain hydrated, therefore the water introduced should neither be evaporated completely, nor should be introduced in excess in order to prevent the flooding of electrolyte [6]. Due to these conditions PEMFC is usually operated at a temperature below 120 °C and typically 80 °C.

Figure 1: Schematic drawing of a hydrogen/oxygen fuel cell and its reactions based on the proton exchange membrane fuel cell (PEMFC).

Source: CARRETTE, L.; FRIEDRICH, K. A.; STIMMING, U. Fuel cells-fundamentals and applications. **Fuel Cells**, v. 1, n. 1, p. 5-39, 2001

Phosphoric acid fuel cell uses concentrated phosphoric acid as electrolyte, which similarly to proton exchange membrane, works as proton conductor; hence the working principle of PAFC and PEMFC is quite similar. The PAFC operates at approximately 150-220 °C. Phosphoric acid is used as electrolyte, because it is the only common inorganic acid that exhibits the required thermal, chemical and electrochemical stability and low volatility at the operating temperature (150-220 °C). The use of concentrated acid (100 %) not only minimizes the water vapor pressure (due to which the water management in the cell is not difficult) but also increases the conductivity of the electrolyte. The acid is usually retained in a matrix, which is based on silicon carbide [7].

In alkaline fuel cell, the electrolyte used is concentrated (85 wt. %) KOH, when the cell is operated at high temperature (~ 250 °C), however the concentration of the electrolyte is decreased to approximately 50 wt. %, when the temperature of the operation is decreased to 120 °C. One of the controversial issues in the AFC is the formation of carbonates, because even the CO₂ present in the atmosphere can react with KOH to form K₂CO₃, thus altering the electrolyte. However, the carbonates build up can be avoided by circulating the KOH instead of using the stabilized matrix [8].

The electrolyte in molten carbonate fuel cell is usually a combination of alkali metal carbonates (Li₂CO₃ and K₂CO₃), stabilized by a ceramic matrix of LiAlO₂. The cell operates at high temperature (typically 600-700 °C), where the carbonates melt to form a highly conductive molten salt with the carbonates ions providing the conduction. Due to high temperature of operation, the MCFC are not prone to CO or CO₂ poisoning, a serious problem in the low temperature fuel cells [9].

Solid oxide fuel cell uses a solid oxide material, usually zirconia (ZrO₂) stabilized with the addition of small amount of yttria (Y₂O₃) as electrolyte. SOFC operates between 800 and 1000 °C, where ZrO₂ becomes a conductor of oxygen ions. As SOFC uses solid electrolyte, therefore the leakage problems due to liquid electrolyte are minimal, hence the SOFC are more stable than MCFC. In addition it has no problems with the presence of trace impurities, water management, or slow oxygen reduction kinetics [10].

A second grouping can be done on the basis of operating temperature for each of the fuel cells. There are thus, low temperature and high temperature fuel cells. The first three types described above, are the low temperature fuel cells, operating at temperature range of 30-220 °C, whereas the last two types are the high temperature fuel cell. The high temperature fuel cells operate at temperature of approximately 500-1000 °C. In low temperature fuel cells

Table 1: The different types of fuel cells that have been realized and are currently in use and under development.

Fuel cell type	Electrolyte	Mobile ion	Operating temperature	Application
Proton exchange Membrane (PEMFC)	PolyperflouroSulfonic acid	H^+	30-100 °C	Transportation, energy storage systems, space, military
Phosphoric acid (PAFC)	Liquid phosphoric acid soaked in matrix	H^+	~ 220 °C	
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	OH^-	50-200 °C	
Molten carbonate (MCFC)	Liquid solution of lithium, sodium and/or potassium carbonates, soaked in a matrix	CO_3^{2-}	~650 °C	Combined heat and power for stationary decentralised systems and for transportation (trains, boats)
Solid oxide (SOFC)	Solid zirconium oxide to which a small amount of yttria is added	O^{2-}	500-1000°C	

(PEMFC, PAFC, AFC) the major charge carriers are the protons or hydroxyl ions, whereas in the high temperature fuel cells (MCFC, SOFC) carbonate ions and oxygen ions are responsible for ionic conduction. An overview of the fuel cells types is given in Table 1. There has been much research effort done on the development of PEMFCs, because they have unique features including low temperature of operation (hence, faster cold start) and a combination of high power density and high energy conversion efficiency. Moreover there is no free corrosive liquid in PEMFCs [11].

1.5. Proton exchange membrane fuel cells

1.5.1. PEMFC Unit cell

In the PEMFC, the combination of the electrodes and the solid polymeric membrane is called membrane electrode assembly (MEA), which is the basic unit of PEMFC stack, as shown in Figure 2 [12]. Each electrode consists of a catalyst layer (CL) and gas diffusion layer (GDL). The CL which varies in thickness from 5 to 20 μm usually contains dispersed Pt catalyst and is mixed with the proton conducting polymer electrolyte to allow protons to flow

Figure 2: Structure of membrane electrode assembly (MEA).

Source: RALPH, T. R.; HOGARTH, M. P. Catalysis for low temperature fuel cells-cathode challenges. *Platinum Metal Review*, v. 46, n. 1, p. 3-14, 2002.

from the electrode to the membrane. The GDL is a porous conducting material made from carbon paper or carbon cloth that allows free passage of the reactant gas to the catalyst layer, while collecting electrons from it at the same time. GDLs are typically 100-300 μm thick and are treated with a hydrophobic substance such as polytetrafluoroethylene (PTFE), in order to avoid flooding of the MEA by improving its water drainage. The membrane, which is typically 25-175 μm thick is designed to conduct the protons while being impermeable to hydrogen or oxygen [13]. Thus the membrane not only conducts the protons, but also prevents the mixing of reactant gases from the anode and cathode compartments. However, a small amount of H_2 and O_2 crossover is observed in conventional PEMFC. The CL is first deposited either on the GDL or the membrane and then the components are hot pressed to form the MEA. The MEA is then placed between two flow field plates to give a single cell. The function of the flow field plates is to distribute uniformly the reactant gases across the faces of the MEA and also to collect current from the MEA, for which they also provide an electronic conductive medium between the anode and cathode [14]. A PEMFC stack may consists of ten to thousands of single cell units in order to provide the desired power output.

In a PEMFC H_2 is fed to the anode side and O_2 is fed to the cathode side. On either side of the MEA the gas flow through the flow field plates and migrate through GDL to CL. The hydrogen oxidation reaction (HOR, reaction 1) takes place on the anode and the oxygen reduction reaction (ORR, reaction 2) takes place on the cathode. The protons pass through the electrolyte membrane from the anode to the cathode and the electrons are forced through an external circuit, also from the anode towards the cathode. The electrons reach the cathode, where they combine with protons and oxygen to produce water [15]. The basic operation of PEMFC is shown in Figure 1.

The overall PEM fuel cell reaction occurs as:

PEMFCs can be used for power generation in portable, stationary and transportation applications, however CO poisoning and insufficient durability of anode electrocatalyst are among the major problems hindering commercialization of PEMFCs.

1.6. CO poisoning of anode electrocatalysts

In PEMFC, if pure hydrogen is used as a fuel, the performance of anode electrocatalyst is excellent with pure Pt catalyzing the hydrogen electro-oxidation. However, the use of pure H₂ as a fuel has a number of limitations, including on-board hydrogen storage, slow refueling of the vehicle using hydrogen and lack of infrastructure required for the distribution of pure hydrogen. Thus it has been proposed that H₂ will be produced on-board by reforming carbon-based fuels such as methanol, natural gas or gasoline. The reformation of these fuels results in a gas mixture of about 75 % H₂, 25 % CO₂ and 1-2 % CO. Following some clean up steps, the CO concentration can be lowered further to about 2-100 ppm [16]. Unfortunately, even such a small concentration of CO in the PEMFC anode feed stream is sufficient for the poisoning of the Pt catalyst employed in the PEMFC anode, thus decreasing the fraction of the catalyst surface that is available for H₂ adsorption and its subsequent electrochemical oxidation [17]. Therefore, overcoming the CO poisoning effect on anode electrocatalysts is of paramount interest for the commercial viability of the PEMFC system.

1.6.1. Methods to mitigate the poisoning effect of CO

Several approaches are used to reduce the poisoning effect of CO on the Pt electrodes employed in the PEMFC anode. The first method to mitigate the CO poisoning is the current pulsing technique [18], in which alternative periodic current pulses are applied to the anode. As a result the potential of the anode shifts periodically in the positive direction, which then oxidized the adsorbed CO on the surface of the electrocatalyst. After termination of the pulse the CO will continue adsorbing on the surface of the catalyst, which means that this method is effective for short period of time. In another method, small amount of O₂ is injected continuously to the anode stream. Usually, 2-5 % O₂ is injected to the anode gas stream, which resulted in high CO tolerance up to a concentration of 500 ppm [19]. In an analogous technique, hydrogen peroxide (H₂O₂) is introduced in to the anode fuel stream. In this case, the O₂ obtained by the decomposition of H₂O₂, oxidize the CO and hence improve the CO tolerance of the anode [20].

Another way of improving the CO tolerance of PEMFC anode is to increase the cell temperature. Leng et al. [21] showed that increasing the working temperature from 25 to 70 °C, the ignition potential of CO oxidation on the PtRu/C catalyst decreases, indicating an improvement in CO tolerance with increase in temperature. They also showed the increased CO tolerance with the increased temperature through cyclic voltammograms for this catalyst. A significant improvement in the performance was observed for the Pt/C and PtMo/C electrocatalysts by increasing the cell temperature from 85 to 105 °C [22]. This indicates the significant effect of temperature on the performance of PEMFC anode supplied with up to 100 ppm of CO. The increased CO tolerance at higher temperature is due to the reduced adsorption of CO on the surface of the catalyst. Unfortunately, increasing the PEMFC temperature beyond 100 °C brings a lot of problems, including membrane degradation and increased degradation of cell components.

Another successful approach of tolerating the CO impurities in the anode gas stream is the modification of Pt catalyst by another element, either by the formation of bimetallic alloy or by the formation of metal oxides or carbides [23,24]. Because the use of CO tolerant electrocatalysts would be more efficient and cause less associated problems, it is therefore, considered as the most promising way for solving the CO poisoning problems in the PEMFCs. Nowadays, much research is addressed to the PtRu alloy as anode electrocatalyst, because the PtRu alloy has a large CO tolerance and chemical stability among the catalysts developed so far [25,26,27]. However, due to the scarcity of Ru, there is a need to reduce the Ru usage and develop catalysts without Ru species. Research done on alloys of Pt with a non-precious metal, such as Sn, Fe, Co, W, Mo etc. or Pt supported on transition metal carbides, have found excellent CO tolerance of these materials when reformat gas is used [23,28,29,30]. Among bimetallic electrocatalysts, the PtMo alloys showed a most promising CO tolerance as compared to the state-of-art PtRu/C catalyst. A wide range of bimetallic PtMo materials has been prepared and studied: single crystals of the true PtMo alloys [31], carbon supported PtMo catalyst and various Pt electrodes whose surface has been modified either with Mo oxides [32] or some other Mo species, such as Mo carbides [33]. For example Kwiatkowski et al. [34] reported that PtMo (4:1) catalyst exhibits a two-to-three fold enhancement in CO tolerance compared to PtRu (1:1). Furthermore, it has been reported that MoOx@Pt electrocatalyst is more effective than PtRu and Pt₄Mo₁ electrocatalysts for CO tolerance up to 250 ppm [35]. Similarly, it has been observed that molybdenum carbide has a high activity for the dissociation of methanol and water, as well as a relatively low CO

desorption temperature of around 330 K [36]. Not only molybdenum carbide, but also tungsten carbide has been proved to be potential electrocatalysts, when reformat fuel is used in fuel cell. Thus, it has been observed that both WC and PtWC exhibit a lower CO oxidation onset potential than pure Pt [37]. The high CO tolerance of these carbide based electrocatalysts is most probably due to the active surface of carbides towards the dissociation of H₂O to produce surface hydroxyl group which are critical for the subsequent oxidation of CO [29]. PtMo/C has not been proved only to be an active electrocatalyst when reformat fuel stream is used, but it is also a strong candidate when the ethanol or methanol is used as fuel in PEMFCs, because due to the presence of Mo, the electro-dissociation of water occurs at lower potential compared to Pt alone. As a result the OH groups produced, oxidized the adsorbed intermediate species to CO₂, which produced during the oxidation of methanol or ethanol.

For methanol electro-oxidation, Ma et al. [38] observed a higher mass activity for Pt-MoO_x/C catalysts compared to Pt/C catalyst. Ordóñez et al. [39] reported an enhanced activity for methanol oxidation on Pt₄Mo₁/C catalyst, showing low onset potential (0.38 V versus RHE against 0.5 V versus RHE for Pt/C) and high current densities for the methanol oxidation reaction.

1.6.2. CO tolerance mechanism

Several mechanisms, including conventional bifunctional mechanism, electronic effect, water gas shift reaction (WGSR) etc. have been reported for the enhancement in the CO tolerance of the bimetallic (Pt-M) electrocatalysts [24,40,41,42]. In the bifunctional mechanism, the CO tolerance of the catalyst is improved by the formation of surface oxides species such as oxy-hydroxides. Due to the presence of these oxides species the CO onset potential then shifts to lower values. Actually, the second element changes the surface properties of the electrocatalyst towards the adsorption of water and oxygen, which first lead to the production of OH_{ad} on the second element and then to the oxidation of CO on the Pt surface, as shown in the following reactions.

This type of mechanism is also called Langmuir-Hinshelwood (L-H) mechanism. For example Watanabe et al. [43] proposed that OH species are nucleated at the Ru in PtRu/C catalyst at lower potential in comparison to Pt in Pt/C catalyst, which then lead to the electrooxidation of adsorbed CO from the surface of the Pt. For the electrocatalysts to exhibit the bi-functional mechanism, the bond energy of the M-O should be of the order 590 kJmol⁻¹, which is the bond energy of Pt-O. The existence of bi-functional mechanism has been confirmed by CO stripping experiments [44].

Another mechanism which also plays an important role in the improvement of the performance of bimetallic anode electrocatalysts in the presence of CO is the electronic effect [45], in which the second element modifies the electronic properties of the Pt. These electronic modifications may affect the interactive properties of the CO with the catalyst and particularly with Pt itself. In fact, the added element changes the electronic properties of the catalyst by changing the 5d band vacancies through the donation or back donation of electrons. These results in weakening of Pt-CO bond strength, leading to desorption of CO from the surface and finally to an increase in cell performance as more catalyst sites are available for H₂ adsorption and oxidation. This effect has been studied by X-ray absorption spectroscopy (XAS) experiment, where an increase in white line intensity was observed for PtRu catalyst compared to Pt alone.

Mukerjee et al. [46] observed an increase in 5-d band vacancies for the catalysts in which the Pt was alloyed to other elements in comparison to Pt/C catalyst. Furthermore, Lausche et al. [47] performed quantum mechanical calculations using density functional theory for the determination of adsorption energies of adsorbates such as H, O and CO. They observed a decrease in the adsorption energies of H and CO on the Pt sites in the presence of Ru atoms. According to XAS experiments not only changes in 5-d band vacancies of Pt were observed due to the addition of second metal, but changes in the spatial atomic structure such as Pt-Pt bond distance, coordination number etc. were also observed. The third type of mechanism responsible for the improvement in the CO tolerance of Pt-M electrocatalysts is the WGSR, where CO in the anode gas stream is oxidized to CO₂ by reacting with water adsorbed on the surface of the electrocatalysts, as shown below:

The WGSR type mechanism has been confirmed by OLMS experiments. Thus one of these mechanisms which occurs on the surface of the electrocatalysts due to the presence of second metal with the Pt may be responsible for the improved CO tolerance of the PEMFC catalysts.

1.7. Stability issues

While a good CO tolerance of the anode electrocatalysts is a key challenge in fuel cell technology, a high level of catalyst stability is also required to tolerate the dynamic operating conditions involved in practical automotive applications. Depending on application, life time requirements of fuel cell vary significantly. According to American department of Energy (DoE), the minimum lifetime requirements for transportation application range from 3000 to 5000 h for cars and up to 20,000 h for buses applications, whereas for stationary application about 40,000 operating h are required. Although the life time requirements for automotive application are considerably less than those of stationary application, the dynamic operating conditions and variations in the voltage due to startup/shutdown make this target very challengeable. Unfortunately, the pre-commercial PEMFC stack doesn't meet these requirements.

Numerous factors, including electrolyte membrane thinning, CL and GDL degradation and carbon support corrosion can affect the durability of PEMFC [48]. Among these, the CL degradation is the most serious factor [49]. Although various types of catalysts have been tested until now, carbon supported Pt and Pt-based alloy are still the most promising electrocatalysts in use due to their greater stability as compared to other catalysts in the corrosive environment of the fuel cell [12,50]. These are the most active catalyst for ORR and are among the most active for HOR. However, their long term stability is still under question [51]. The factors responsible for CL degradation include: 1) Pt sintering and dissolution, 2) contamination by impurities and 3) Pt particle growth and agglomeration [52,54,68]. Of all these factors, the most dominant mechanism for catalyst layer degradation is Pt particle growth and agglomeration, as shown previously [55]. In order to reduce the high surface

energy, nanoparticles have tendency to agglomerate into bigger particle. As the particles grow, their surface energy decreases and the growth process simultaneously slow down. Pt nanoparticles can experience more severe agglomeration during long term operation or accelerated stress tests. This can result in a loss of active surface area of the catalyst and consequently performance degradation in PEMFC. Ferreira et al. [53] analyzed degraded MEA after long term operation of 2000 h and supposed that small particles may dissolve in the ionomer phase and redeposit on the surface of the larger particles in a process, called Ostwald ripening. Meier et al. [56] described that during the Ostwald ripening process the Pt particles are transported through the electrolyte and the electrons through the carbon, and is the main reason responsible for particles growth.

Migration of Pt nanoparticles is another main reason responsible for loss in ECSA and consequent performance degradation of MEA. Several studies have shown that Pt particles detach from the carbon support and accumulate on the interface between the CL and electrolyte membrane, which lead to limited catalyst activity because of the poorer proton transport at the interface [57,58,59]. The final reason for the increase of particle size and decrease in catalytic activity is the formation of surface oxides at the anode [50,60,61], which blocks the H_2 to reach the Pt. Whatever mechanism the particle growth follows, it is an important factor in the degradation of CL and leads to a decrease in Pt mass activity, particularly during voltage cycling and long term operation.

In the case of Pt-M alloys (where M = Mo, Ru, W, Fe etc.), the acidic environment of the fuel cell may cause a partial loss of M from the alloy itself, possibly reducing catalytic activity. For example, E. Antolini [62] observed the dissolution of Ru from the Pt-Ru anode catalyst and its presence in the cathode side. Similarly, it has been shown that W dissolved from the PtW/C anode and migrated through the electrolyte membrane towards the cathode [28].

In addition carbon corrosion also plays an important role in the degradation of PEMFC anode electrocatalyst. Usually carbon supported catalysts are used in the PEMFCs due to their reasonable stability, good porosity and electronic conductivity [63,64]. Electric current is generated at the metal nanoparticles, which are randomly dispersed on high surface area carbon substrate. The structural morphology and appropriate dispersal of these metal nanoparticles on the support material make the fuel cell operation feasible. The support material should not only have the dispersion effect, but also must have adequate interaction with the metal nanoparticles. The interaction effect can alter the properties of the

electrocatalysts, either by modifying the electronic properties of the Pt in the metal particles or by changing their size and shape. Working together, these effects could increase the activity of the catalyst by increasing the number and the activity of metallic sites. In addition to a high surface area and sufficient electrical conductivity, a support for a fuel cell catalyst must have sufficient durability to tolerate the corrosive environment of the fuel cell. Unfortunately, the carbon, the most commonly used support is unstable under strong electrochemical oxidizing conditions of the fuel cell for long term operation.

In the PEMFC two factors are responsible for the corrosion of carbon support: 1) fuel starvation and 2) start up and shut down processes. During fuel starvation when H₂ is no longer sufficient to provide the expected current, the potential of anode increases and that of cathode decreases, until the condition of cell reversal is reached, where the potential of anode is greater than that of cathode. This leads to the dissociation of water and oxidation of carbon to provide the necessary protons and electrons for the ORR, according to the following reactions.

For example Taniguchi et al. [65] observed a severe area loss of electrocatalyst and decline in performance of the cell caused by carbon corrosion due to fuel starvation. Similarly, Knights et al. [52] investigated the polarization of fuel cell under the condition of fuel starvation. They observed a drop in cell voltage and detected the presence of O₂ on the anode side by gas chromatography (GC). As a result of carbon corrosion the number of surface sites available from support to anchor the metal nanoparticles decrease, which eventually cause the structural failure of the electrode. A second kind of carbon corrosion can result from continuous start up and shut down processes. During its life time, a fuel cell may experience up to 30,000 start up and shut down cycles. Both these processes can result in the corrosion of carbon due to the presence of H₂ and O₂ simultaneously in the anode fuel stream. It has been stated that, when a fuel cell system is turned off, the H₂ supply to the system is cut off and air will leak slowly to the anode. Through this process, the anode compartment will be filled by air, if the fuel cell is kept shut down for long period. The air will be replaced by H₂, when the fuel cell is started, which can lead to carbon corrosion.

The carbon oxidation/corrosion can cause not only the agglomeration of metal particles, but can also lead to the formation of oxygen containing groups such as carbonyl, carboxyl, hydroxyl etc. on the surface of the catalyst [66,67], which decreases the conductivity and weakens the interaction of metal nanoparticles with the support, leading to accelerated sintering of the metal particles. Therefore it is important to assess the degree of catalyst stability under conditions that simulate the real-life PEMFC anode operating conditions.

Up to the end of 20th century, the catalyst support in low temperature fuel cells was limited only to carbon black. However, in the last decade the trend has been changed, and research has been started on new carbon and non-carbon materials, aiming to improve the electrochemical activity and stability of the catalysts. For example, graphitized carbon and multi-walled carbon nano-tubes have been observed as more stable supports than the carbon black for the fuel cell catalysts [68,69]. Dou et al. [70] have reported carbon free WO₃ nanoclusters, as a highly electrochemical stable support compared to Vulcan XC-72.

In addition, transition metal carbides have been studied as potential electrocatalyst supports, because of their catalytic activities for many chemical reactions including hydrodenitrogenation, hydrodesulfurization, methanol steam reforming and WGSR [71,72,73]. These carbides can be produced having large surface area and catalytic properties resembling those of the Pt-group metals (PGMs) [74,75]. If used as support, carbides help to increase the dispersion of precious metal [76]. In particular, molybdenum carbide (Mo₂C) and tungsten carbides (WC) have been investigated as anode electrocatalyst for PEMFCs, although their catalytic activity for H₂ electro-oxidation is not high enough to meet the requirements for fuel cell applications. However, the catalytic activity of these carbides can be noticeably improved by the addition of Pt. In a recent study conducted to evaluate the use of molybdenum carbide as electrocatalyst in fuel cell anodes, it has been reported that Pt-Mo_{carb} supported on carbon black has shown a superior activity for methanol electro-oxidation in comparison with Pt supported on carbon [30]. Moreover, Weigert et al. [77] observed that Pt-modified Mo-C has enhanced activity and stability compared to Pt supported on carbon. Likewise, there have been recent studies conducted to evaluate the use of tungsten carbide as catalyst support for use in fuel cells and it has been shown that Pt supported on tungsten carbide have superior activity in both the methanol electro-oxidation and ORR [78,79]. Additionally, Chhina et al. [80] reported a higher activity and stability for oxygen reduction reaction before and after 100 oxidation cycles for Pt/WC as compared to Pt/C. In another

study, it has been observed that Pt supported on tungsten carbide shows higher activity for electrochemical oxidation of methanol than a commercial carbon supported PtRu electrocatalyst [81]. Lee et al. [82] reported that Pd/WC shows improved activity for the electro-oxidation of methanol as compared to a Pd/C catalyst in an alkaline media. Similarly, in the research work conducted by Moon et al. [83], it has been demonstrated that Pd supported on mesoporous tungsten carbide showed a more negative peak potential compared to Pd/C in the CVs for methanol electrooxidation. They also evaluated the stability of these electrocatalysts in alkaline solution containing methanol and reported only 2.2 % decrease in current density for Pd/meso-WC after stability test compared to a decrease of 26 % for Pd/C.

In subsequent study, it has been shown that tungsten carbide only has low activity for methanol and hydrogen oxidation [84]. The hydrogen oxidation activity of WC-based anode in absence of noble metals was evaluated by Yang and Wang [85]. They observed that WC has very low activity towards hydrogen oxidation. However, the activity could be improved significantly by adding a small amount of Pt to tungsten carbide. Hence, in the work performed by Dong and co-workers, the Pt/WC catalyst showed two times higher activity per mass of Pt for hydrogen oxidation compared to a commercial Pt/C [29]. Similarly, Kelly et al. [86] investigated the hydrogen evolution activity of Pd supported on tungsten and molybdenum carbide. In their work a superior activity was noted for Pd/C in contrast to bare carbides. Nevertheless, only the addition of monolayer of Pd to these carbides doubled the values of corresponding current density for the resultant carbide based electrocatalysts. Furthermore, the activity and stability of Pt supported on tungsten carbide has been tested for hydrogen evolution and oxidation reactions by Liu and Mustain [87]. Although they found a very little difference in the activity of Pt/WC and Pt/C catalysts for hydrogen evolution reaction, the stability of Pt/WC was far better than that of Pt/C. A loss of only 4 % in activity was observed for Pt/WC which was very small in comparison to loss in activity of more than 20 % for Pt/C.

Although carbon supported PtMo electrocatalysts have shown a CO tolerance up to threefold the tolerance of the state-of-the-art PtRu/C catalysts [88], their long term stability regarding the CO poisoning is under discussion. It has been shown that bimetallic PtMo/C electrocatalysts are inherently unstable and suffer from the gradual loss of Mo due to its dissolution [22,89]. One of the major approaches to improve electrocatalyst activity and stability is the thermal treatment. It has been observed that heat treatment can affect the metal particle size, particle distribution and interaction of support with the metal particles [90]. In

addition heat treatment has significant impact on the fundamental properties of the catalyst, such as the acid-base and redox properties of the support, the number of catalytic sites and distribution of metal particles on the support [91]. It has been shown that particle size and catalyst structure can largely affect the reduction of the molecular oxygen on the catalyst. Since the heat treatment has significant effect on the particle size, therefore it can significantly enhance the catalytic activity of Pt/C catalyst for ORR [92]. A similar behavior was shown for CO oxidation, where the catalytic activity of Pt/C catalyst improved significantly by heat treatment [90]. In the case of carbon support, Prado-Burguete et al. [93] investigated the effect of heat treatment in the presence of helium on porous texture of carbon and observed a significant decrease in its meso and micro porosity. Results showed that heat treatment in the presence of H_2O_2 not only increase the dispersion of Pt particles on carbon, but also increased the amount of oxygen containing species on the surface of the support [94]. These oxygen containing groups facilitate the distribution of metal precursor by increasing the wettability of carbon particle surface during the impregnation and reduction steps of the catalyst preparation.

In addition, the thermal stability of catalyst heat treated in the presence of H_2O_2 was much better than that of only heat treated. Studies have shown that heat treatment could stabilize the carbon support against electrochemical corrosion. In the work performed by Stonehart [95], it has been shown that heat treated Pt/C is more stable than untreated Pt/C catalyst. The author stated that the greater stability of the heat treated catalyst is due to stronger interaction between the metal particles and basic anchoring sites than untreated catalyst. Heat treatment of Pt-M (M = Mo, Ru, W, Fe, Sn etc) alloy electrocatalyst at high temperature leads to a better formation of Pt-M alloy by decreasing the Pt-Pt distance and affecting the d-band vacancy of Pt, hence increasing the catalytic activity of catalyst [96,97]. As the heat treatment causes an increase in particle size of the catalyst which results in decrease of the catalyst active area, consequently the heat treatment could have negative effect on the catalyst mass activity. However, as the heat treatment also brings about changes in the lattice structure, therefore the negative effect produced by increase in particle size may be overcome by the changes in lattice structure.

Several heat treatment techniques, including traditional oven/furnace heating [98], microwave heat treatment [99,100], plasma thermal treatment [101,102] and ultrasonic spray pyrolysis [103] have been applied to prepare and treat PEM fuel cell electrocatalysts. However, the most commonly used is the traditional oven/furnace heating, which involves

heating the catalyst in a tubular furnace or oven in the presence of an inert (N_2 , Ar, or He) or reducing (H_2) atmosphere, in the temperature range of 80-900 °C for 1-4 h [104].

In the present work, traditional oven/furnace heating technique was used for the heat-treatment of the PtMo/C catalyst for the purpose of improvement in activity and stability of this catalyst. Similarly, molybdenum and tungsten carbides were used as supports for PEMFC anode electrocatalysts, in order to improve the performance of PEMFC anodes against harsh conditions of operation [105,142].

2. OBJECTIVES

In this work, carbon supported PtMo (60:40 atomic proportion) catalyst, prepared by the formic acid reduction method, was heat treated in the temperature range of 400-700 °C, by the traditional oven/furnace heating technique in the presence of reducing (H₂) atmosphere for 1 h. The purpose of the present study was to improve the activity and stability of PtMo/C catalysts, especially against load changes. A potential cycling protocol of cyclic voltammetry at a scan rate of 50 mVs⁻¹ ranging from 0.1 to 0.7 V was applied to the anode, to stimulate load changes during fuel cell operation. To evaluate the stability of the catalysts, the performances of membrane electrode assemblies (MEAs) was measured before and after potential cycles at intervals of 1000 potential cycles and the polarization curves were compared. In a second attempt to improve the stability, molybdenum carbide and tungsten carbide were used as support of Pt electrocatalysts for hydrogen electrooxidation in the presence of 100 ppm of CO for PEMFC anodes. The results obtained were then compared with those obtained for carbon supported PtMo, PtW and Pt electrocatalysts. All the electrocatalysts obtained were characterized physically by utilizing various characterization techniques, such as temperature programmed reduction, powder X-ray diffraction, energy dispersive spectroscopy, X-ray absorption, transmission electron microscopy, scanning electron microscopy and wavelength dispersive spectroscopy were performed to know about the physical properties of the electrocatalysts. All the electrocatalysts were also characterized electrochemically by polarization measurement, cyclic voltammetry, online mass spectrometry and CO stripping experiments. Cyclic voltammetry was used as degradation testing technique to evaluate the electrocatalysts stabilities.

CHAPTER II

MATERIAL AND METHODS

3. MATERIALS AND METHODS

3.1. Preparation of electrocatalysts

3.1.1. Preparation of PtMo/C electrocatalysts

A PtMo/C (60:40 atomic proportion, 20 wt. % metal/C) catalyst was prepared by the formic acid reduction method [44,105,106,107] which consisted of simultaneous reduction of dihydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich) and tetrahydrate ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Mallinckrodt], using formic acid (HCOOH , J. T. Baker) as reducing agent in the presence of carbon (Vulcan XC-72, Cabot). Briefly, the method consists of the addition of carbon powder into a solution of formic acid of known concentration. After dispersion in the ultrasonic bath for about 20 minutes, the mixture is heated on a water-bath. When the temperature is reached to 80 °C, the precursor solutions of known concentration are added to it in a portion of 1 mLmin⁻¹. After the addition of metals precursors, the mixture is filtered, washed several times with Mili-Q water to remove the impurities and then dried at 100 °C in oven for two hours.

3.1.2. Preparation of Pt/Mo₂C/C electrocatalysts

The molybdenum carbide support with 30 wt. % Mo/C was prepared by sonicating a slurry of molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$, Aldrich) and carbon powder (Vulcan XC-72R) in hexadecane ($\text{C}_{16}\text{H}_{34}$, Synth), with a high intensity ultrasonic horn at 90 °C for 3 h. The resulting mixture was filtered, washed several times with purified pentane (C_5H_{12} , Aldrich) and heated at 90 °C to yield black powder. The powder was then transferred to a tubular quartz reactor and placed in a furnace. It was exposed to an argon flux and heated up to 100 °C for 1h. The gas was then changed for a 1:1 CH_4/H_2 mixture and the temperature was increased at a heating rate of 5 °C min⁻¹, firstly until 300 °C for 1h, secondly until 400 °C also for 1h and finally until 500 °C for 12 h, in order to carburize the black powder [108,109].

Both Pt and PtMo (20 wt. %) were produced and deposited on Mo₂C and Vulcan XC-72R by the formic acid reduction method as described above.

3.1.3. Preparation of Pt/WC/C electrocatalysts

The tungsten carbide supports with different W/C wt. percentages (10, 20 and 30) were prepared by a simple impregnation method [110]. Briefly, the tungsten precursor (WCl₆, Aldrich) and carbon black (Vulcan XC-72) were added in to ethanol and then the composite was impregnated for 3 h at room temperature. The mixture was then heated at 70 °C, until the ethanol was evaporated completely. The resultant solid was transferred in to a quartz reactor, placed in a tubular furnace and heat treated under CH₄/H₂ atmosphere at 800 °C for 3 h to give the tungsten carbide, which was passivated using a 1 % O₂/Ar mixture for 3 h, prior it was taken outside the quartz reactor. Pt (20 wt. %) was deposited on these carbide supports by the formic acid reduction method, as described above. These catalysts were then designated as Pt/WC/C10, Pt/WC/C20 and Pt/WC/C30, where the numbers represent the wt. % ratios. For the purpose of comparison, PtW/C (60:40 atomic proportions) was prepared by the same formic acid method, maintaining the metal content at 20 wt. %. Pt supported on Vulcan XC-72 carbon also with 20 wt. % metal/C was supplied by E-TEK.

3.2. Preparation of gas diffusion electrodes

The gas diffusion electrodes (GDEs) are used in the fuel cells due to their high surface areas and easy approach of reactant gases to the electrocatalyst particles [111]. The GDEs consist of a carbon cloth upon which is deposited the gas diffusion layer and a catalyst layer. The gas diffusion layer was formed by applying a mixture of carbon powder (Vulcan XC-72, Cabot) with 15 wt. % of polytetrafluoroethylene (PTFE, TE 306A, Dupont) on to both sides of a carbon cloth substrate (PWB-3, Stackpole), using a loading (carbon+PTFE) of 3 mg cm⁻² on each face. The carbon cloth was first heat treated at 450 °C in air atmosphere for 1h and then treated with 25 % V/V nitric acid solution also for 1h in order to decrease its

hydrophobicity. A mixture composed of 15 % PTFE and 85 % carbon powder was then placed in an ultrasonic bath for about 10 min. in order to obtain a homogenous suspension. The pH of this suspension was maintained at 3 by the drop wise addition of 0.5 M H₂SO₄. It was then filtered under vacuum on both sides of pre-treated carbon cloth followed by heating at 280 °C for 30 min. to remove the dispersant and finally it was sintered at 300 °C for half hour.

The catalyst layer was prepared from an homogeneous suspension formed by Nafion® solution (Aldrich, 5 wt%), the electrocatalysts (PtMo/C, Pt/Mo₂C/C, PtMo/Mo₂C/C, Pt/WC/C and PtW/C) in the case of the anodes and Pt/C in the case of the cathode and isopropanol. Appropriate amount of catalysts, Nafion® solution and isopropanol were mixed, homogenized in an ultrasonic bath for 10 min. and was finally dried in air to obtain a solid material. This solid material was then mixed with isopropanol to produce an ink, which was then applied by a brushing procedure on one face of each gas diffusion layer. Finally, these electrodes were dried in an oven at 90 °C for 1 h. The metal load was 0.4 mg cm⁻² for both, anodes (PtMo/C, Pt/Mo₂C/C, PtMo/Mo₂C/C, Pt/WC/C and PtW/C) and cathode (Pt/C, E-TEK) with the total area of the electrodes equal to 4.62 cm². The quantity of Nafion® used was 35.5 wt. % of total mass of catalyst layer.

3.3. Pre-treatment of proton exchange membrane (PEM)

The most commonly used membranes in PEMFC are Nafion® which are made of a perfluorosulfonic acid (PFSA) polymer. The skeleton of membrane consists of CF₂ groups to which hydrophilic SO₃H groups are attached at certain points. Where the CF₂ groups are responsible for the chemical stability of the membrane, the SO₃H groups take account of the conduction of protons through membrane. Usually these membranes are commercially available from DuPont with the thickness varying from 25-175 μm. In this work Nafion®115 membranes (Dupont) of 127 μm thickness was used, which was pre-treated with an aqueous solution of 3 % H₂O₂ at 80 °C for 1 h in order to remove the organic impurities. The process was repeated four times using ultra-pure water for the removal of traces of H₂O₂. It was then treated with 0.5 M H₂SO₄ solution at 80 °C during 1 h for the removal of metallic impurities.

Finally the membrane was washed several times with distilled water and placed in the bottle containing Mili-Q water until its use.

3.4. Preparation of membrane electrode assembly (MEA)

MEA was prepared by hot pressing the anode and cathode on both sides of a Nafion® 115 membrane (Dupont) at 125 °C and 5 MPa for 2 min. The MEA was then placed between two high density graphite plates in which serpentine type gas distribution channels were machined. Finally, the system was compacted by aluminum plates that serve as the current collectors. The mounted cell is monitored by a fuel cell station, which allows controlling the temperature, humidification, pressure, flow of the reactant gases and cell potential.

3.5. Physical characterizations

3.5.1. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) is a commonly used technique for the characterization of catalyst including metal oxides, mixed metal oxides and metal oxides dispersed on a support material. From TPR analysis one can yield information about the reducibility of oxidative nature of the catalyst surface. In TPR analysis a reducing gas mixture (usually 3-17 % H₂ diluted in an inert gas such as Ar, N₂ or He) is allowed to flow over the sample. Changes in the thermal conductivity of the reducing gas mixture are then measured by a thermal conductivity detector (TCD). Plots of TCD signal vs. time or temperature can provide qualitative or quantitative information of the oxides species present on the surface of the electrocatalysts [112]. TPR analysis of the PtMo/C catalyst was performed by using a Micromeritics AutoChem II Chemisorption Analyzer. The reducing gas mixture used was 10 % H₂/Ar. The H₂ consumption was measured by a TCD and a liquid N₂/isopropanol bath was used to remove the moisture formed during hydrogen reduction. A catalyst sample of 16 mg

in weight, a flow rate of reducing gas of 10 mL min⁻¹ and a temperature ramp of 10 °C min⁻¹ from 0 to 1000 °C was used. On the basis of the peaks obtained in the TPR profile, the PtMo/C catalyst samples were then heat-treated under flowing H₂ atmosphere, at several temperatures, ranging from 400 to 700 °C for 1 h, with a ramping rate of 5 °C min⁻¹.

3.5.2. *Energy dispersive X-ray spectroscopy (EDX)*

The working principle of EDX is the interaction of electron beam with matter in the sample. When high energy electron (Typically 20 keV) strikes the ground state electron at sample surface, the electrons from the ground state jumped to an unbound state. A photon of energy equal to the energy difference between the two levels is emitted when the space created by the exited electron is filled by an electron from the outer shell. As the energy difference between the two atomic levels is the characteristic of the atomic structure of the each element, therefore the emitted photons take information about the element from which they are emitted. The photons are emitted almost in all direction and can be detected by EDX detector which is normally a silicon crystal and is cooled by liquid nitrogen [113]. The EDX technique was used to determine the metal content of Mo₂C/C, WC/C, metal loading (Pt, Mo and W) and Pt:Mo, Pt:W atomic ratio. A scanning electron microscope LEO, 440 SEM-EDX system (Leica-Zeiss, DSM-960) with a microanalyser (Link analytical QX 2000) and a Si (Li) detector a 20 keV incident electron beam was used for this purpose.

3.5.3. *X-ray diffraction (XRD)*

When a beam of X-rays strikes an atom, two scattering processes take place. The electrons “which are tightly bound” start oscillation and emit X-rays of the same wavelength as that of incident beam. This is called coherent scattering. On the other hand the loosely bound electrons scatter part of the incident beam and increase its wavelength in the process which is called incoherent scattering. Both these processes occur at the same time and in all directions. If atoms are arranged in a regular array like crystal, then diffracted beams are

produced in a process where the coherently scattered radiation are reinforced in one direction and cancelled in other directions. X-ray diffraction is therefore a result of reinforced coherent scattering. Diffraction pattern thus consists of peaks formed by the X-ray intensity of the reinforced coherent scattering. For the diffraction to occur, the wavelength of the incident beam should be of the order of distances between the planes of the atoms. No interaction will occur if the wavelengths are too large.

For example if parallel beam of X-rays AX and BY enter the plane at an angle θ , both these rays are scattered by atoms X and Y and can appear as a single beam only if they reinforce each other. This is known as constructive interference which can occur only if the path lengths of the interfering beams vary by an integral number of wavelengths. In other words the difference in path lengths of two beams must be zero or whole number of wavelength. If the ray B scattered by atom Y travelled a distance of GY + YH more than the ray scattered by atom X, then

$$GY + YH = n\lambda = 2d\sin\theta \quad (10)$$

This is known as the Bragg's law. Through this equation, lattice parameters of the crystallites can be calculated [114]. The XRD analysis can also provide information about the crystallite size in the nanometer range by using a simple equation developed by Debye-Scherrer [115],

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \quad (11)$$

where B is the peak width, L the crystallite size, λ the wavelength, θ the Bragg angle and K the constant of proportionality, known as the Scherrer constant. The K depends on how the width is determined, the shape of the crystal and the size distribution. It can be observed from the above equation that the peak width is inversely proportional to crystallite size which means that as the crystallite size gets smaller, the peak gets broader. In this work crystallite size and lattice parameters, were determined by X-ray diffraction (XRD, RIGAKU model RU200B) in the 2θ range from 10 to 90° and using CuK α radiation.

3.5.4. X-ray photoelectron spectroscopy (XPS)

In X-ray photoelectron spectroscopy (XPS) soft X-ray interacts with the sample surface up to the penetrating depth of few nanometers. As a result of this interaction, photoelectrons are emitted from the sample surface through photoelectric effect. The kinetic energy (K.E) of these electrons is given by the equation [116]:

$$K.E = h\nu - BE - \phi_s \quad (12)$$

where

$h\nu$ is the energy of photon

BE the binding energy of the atomic orbital from which the electrons are emitted and

ϕ the spectrometer work function

The vacancy produced by the surface electron in the inner level after interaction with X-ray can be filled by electron from higher energy level. As a result of this electron transfer, either X-rays or an electron (Auger electron) of energy equal to the energy difference between the two electron levels are emitted. Both the Auger electron and x-ray radiation have characteristic energy and can be used for the determination of elements. From XPS spectra, one can yield information not only about surface elements but also about their bonding energies. In addition concentration of elements can also be obtained by analyzing peak intensity. XPS is an important method for fuel cell research, because information about degradation processes occurring in the fuel cell components and changes in chemical states of elements can be obtained through such technique.

XPS measurements were conducted for the investigation of surface oxidation state of the catalysts. XPS studies were conducted at the National Synchrotron Light Laboratory (LNLS) on a SPECS (spectrometer-Phoibos HSA3500 MCD9 150) equipped with a InSb (111) monochromator and X-rays with energy of 1840 eV. The energy was calibrated to give a binding energy of 84 eV for the gold 4f_{7/2} region. The instrument was programmed for the passage of 20 eV energy, with the energy step of 0.1 eV and acquisition time of 200 ms.

3.5.5. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is an important technique for characterizing microstructure of material. In TEM a beam of electrons interact with the ultra-thin specimen as it is transmitted through. The image which is formed from this interaction can be magnified and focused on the imaging device. The difference between the TEM and optical microscope is that, in light microscope visible light is used, whereas in TEM high energy electrons (100-1000 keV) are used. The wavelength corresponding to this energy range is very shorter (0.0037-0.00087 nm) than the wavelength of visible light, therefore the resolution limits of TEM is almost at atomic level. In addition to be transparent to the electrons the sample for TEM must be sufficient thin (below 100 nm), so that enough electrons be transmitted to form an interpretable image on photographic film. Thus, the thinner the sample the better will be the TEM image [117].

In this work the sample was prepared by the dispersion of catalyst in isopropanol using the ultrasonic bath. It was then transferred to the carbon film supported by copper grid using thin porous coating procedure (TPC). Simple TEM analysis of various catalysts was carried out in order to know about the particle sizes of the catalysts as well as their size distribution. In addition, to study the effect of operating conditions on the catalyst morphology, TEM images of the catalysts sample were obtained after testing in the fuel cell. These analyses were performed, using Transmission electron microscopy (TEM, JOEL 2100 transmission electron microscope).

3.5.6. X-ray absorption spectroscopy (XAS)

When the X-rays strike a sample, there is possibility of one of these processes to occur. These radiations are either scattered or absorbed by the electrons and will be excited. When a monochromatic X-ray beam of intensity I_0 passing through a sample of thickness t , these x-rays are absorbed by the sample according to Beer's Law [118]:

$$I = I_0 e^{-\mu t} \quad (13)$$

where I is the X-ray intensity transmitted through the sample and μ the absorption coefficient, which depends upon the sample density P , the atomic number Z , atomic mass and energy of

X-ray. At certain energy of incident X-ray, there is a sharp rise in absorption and give rise to absorption edge. Each such edge occurs when incident X-ray has energy equal to that of binding energy of core electron to cause its excitation to continuum state. The edge energies correspond to the binding energies of the electrons in the K, L, M, etc, shells of the absorbing element. The absorption edges are labeled in the order of increasing energy, K, L_I, L_{II}, L_{III}, M_I, and so on. Both K and L levels can be used in the hard X-ray regime (5 and 35 keV), thus allowing most elements to be investigated by XAS. The excited state of the atom with one of the core levels left empty and a photoelectron will ultimately decay soon after absorption. XAS can be measured either in the fluorescence or in the transmission mode. In the former case a higher energy core level electron occupy the deeper hole created by the emission of electron after absorption of X-rays. In this process X-ray of well-defined energy is emitted and is characteristic of the atom and can be used to identify and quantify the atoms in

Figure 3: Decay of the excited state of an atom: X-ray fluorescence (left) and Auger effect (right).

Source: NEWVILLE, M. **Fundamentals of XAFS**. Chicago: University of Chicago, 2004. 3 p.

a system. For example, K_α fluorescence line is emitted when an electron from L shell drops in to K shell, as shown in Figure 3. In the transmission mode, an electron from higher energy electron level drops to the core hole and a second electron is emitted to the continuum, as

shown in Figure 3. An X-ray absorption spectrum is generally divided into two distinct portions: X-ray absorption near edge structure (XANES) usually with 30 eV of the absorption edge and the extended X-ray absorption fine structure (EXAFS), in the region between 50 and 1000 eV above the absorption edge [118]. In the XANES region transitions of core electrons to non-bound levels take place, due to which a sudden increase of absorption is observed, whereas in the EXAFS region the ejected photoelectrons experience multiple scattering from the electrons of neighboring atoms. Both these regions of XAS spectrum have been identified in the Figure 4.

In this work XAS analysis (beamline D041 XAFS1 at the Brazilian Synchrotron Light Laboratory, LNLS) in the transmission mode was used to determine the electronic properties of Pt in the electrocatalyst samples focused on the XANES region of the Pt L_3 absorption spectra, that can provide information about changes on the electronic structure of the Pt 5d-band and thus on the reactivity of the catalysts. These experiments were conducted by using a

Figure 4: XAS spectrum with the identified XANES and EXAFS regions.

Source: NEWVILLE, M. **Fundamentals of XAFS**. Chicago: University of Chicago, 2004. 3 p.

homemade spectro-electrochemical cell which enables to set virtually the same humidification, temperature and gas flux as in a fuel cell [42,107,119]. The working electrodes consisted of pellets formed by the dispersed catalyst materials agglutinated with Nafion® and containing 6

mg Pt cm⁻². The Pt cathode fed with hydrogen was used as the reference electrode and the counter electrode was a Pt screen with a cut in the center in order to allow the free passage of the x-ray beam. These experiments were performed with the electrodes polarized at 50 mV vs. RHE.

3.5.7. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) can be successfully used to examine the morphological changes that occur in the various components including CL and GDL of the PEMFC after long term operation or under accelerated stress tests. Usually, SEM is combined with EDX and is a very useful technique in inspecting the modification of fuel cell catalyst layer due to particles agglomeration, migration and washing out of particles. In SEM “like TEM” electrons are used to envision the structural properties of the material under investigation. When a beam of nearly monochromatic electrons hit the sample surface, the primary electron beam is scattered by the atoms when it enters the sample, which leads to an energy loss of these primary electrons. Three different types of electrons and radiation are emitted when the loss in the energy of primary electrons results to an increase in the energy of the surface electrons: 1) back scattered electron (BSE), 2) secondary electrons (SE) and electromagnetic radiation (EMR). Since the energy range of the BSE is in the same range of PE due to elastic scattering, therefore these BSE contain information about structure and composition of the sample. The SEs are emitted from the sample surface in the inelastic collision when the PEs are decelerated by the sample matter. Since the energy of the SEs is very low (few electron volts), therefore they are generated near the surface and thus contain more information about the sample surface than BSE [113].

Scanning electron microscopy (SEM) of cross sections of the MEAs (membrane electrode assemblies) were performed, in order to investigate the loss of Mo from the PtMo, Pt/Mo₂C/C and PtMo/Mo₂C/C catalysts and its migration to the electrolyte membrane and cathodes. To this purpose, samples of the new and cycled MEAs were cut transversely with scissors, then they were mounted on aluminum sample holder, and finally they were coated with a carbon layer, in order to increase their surface electrical and thermal conductivities. The SEM analysis was performed using a SIGMA (Carl Zeiss) field emission scanning

electron microscope (FE-SEM).

3.5.8. Wavelength dispersive Spectroscopy (WDS)

Both the electron probe microanalysis techniques (energy dispersive and wavelength dispersive spectroscopy) are used to identify the constituents of elements by using characteristic X-ray emitted from the sample and hence most SEM instruments are either equipped with EDS or WDS spectrometer. Where the EPMA-EDS is a relatively quick and simple process, the EPMA-WDS takes longer time and has complex set up. However, the combination of sensitivity and better spectral resolution makes the EPMA-WDS technique to detect elements at typically lower concentration than EPMA-EDS. The WDS spectrometer counts the produced X-rays at higher rate, which are produced at higher beam currents. Due to poor resolution of EDS spectrometer, usually the overlaps of adjacent peaks occur, which becomes a serious problem if the overlapped elements are present in trace amounts. This problem can be solved by using WDS spectrometer to examine the overlap by increasing the sensitivity for trace elements [120]. The procedure for sample preparation is exactly the same as for SEM analysis. This analysis was done with a JEOL JXA 8230 electron probe microanalyzer, using a wavelength dispersive spectrometer and a PETJ analyzer crystal. Both SEM and EPMA-WDS studies were carried out in the Laboratorio de Microscopía Electrónica y Análisis por Rayos X, from the Facultad de Matemática, Astronomía y Física (FAMAF), Universidad Nacional de Córdoba, Argentina.

3.6. Electrochemical characterizations

3.6.1. Polarization curves

The performance of a fuel cell can be characterized by measuring its polarization curve, which is simply the plot of cell voltage vs. current density. The polarization curve

yields information on performance losses in the fuel cell under operating condition. Certain parameters such as composition, flow rate, temperature and relative humidity, which affect the fuel cell performance can be characterized and compared by measuring the polarization curve. However, they have some disadvantages such as; 1) they can't provide information about the individual component of the fuel cell, 2) they can't be measured during normal operation of fuel cell 3) they take sufficient time to complete and 4) they fail to provide information of flooding and drying inside the fuel cell [121]. The ideal polarization curve for a fuel cell has three main regions including; activation polarization, ohmic polarization and concentration or mass transport polarization, as shown in Figure 5.

In activation polarization, at low current densities, the cell voltage falls rapidly. This is mainly due to sluggish kinetics of oxygen reduction reaction occurring at the cathode. Activation polarization is the most important irreversibility and causes of voltage drop in the fuel cell, however at higher temperature it becomes less important. In the region of ohmic polarization, at intermediate current densities, there is voltage loss due to significant ohmic resistance. Typically in this region, the cell voltage decreases almost linearly with the current density. The origin of ohmic polarization is the diffusion of the fuel and conduction of electrons from the anode through the electrolyte membrane to the cathode. Both these processes are producing no current, since the fuel/electron will react with oxygen directly to produce the water. The third and last reason for the voltage drop in polarization curve is the mass transport or concentration losses, which usually occurs at high current densities. In the region of high current densities, the cell voltage drop significantly, due to the slower transfer speed of reactants and products than the rate of reaction rate. Figure 5 also shows the difference between the theoretical cell potential and operational cell potential. Normally, the theoretical cell potential is above the open cell potential due to crossovers of undesired species from the one electrode to another through electrolyte membrane and internal currents.

Fuel cell polarization measurements were carried out galvanostatically with the cell at two different temperatures (85 and 105 °C). For 85 °C the gases were saturated with water at 100 °C and 2 atm for the anode and at 90 °C and 1.7 atm for the cathode, whereas at 105 °C the gases were saturated at 120 °C and 3 atm for the anode and 110 °C and 2.7 atm for the cathode. The system was first maintained at an initial potential of 0.7 V in pure H₂, for 2h, and then at 0.8 V in H₂/100 ppm CO, also for 2 h, to reach the steady state before the data acquisition at both the temperatures. In these experiments the cathode was constantly fed with O₂.

Figure 5: Typical polarization curve for PEMFC.

Source: ZHANG, D.; YUAN, X.; MA, Z. **Polarization Curve**. New York: CRC, 2012. v. 1, p. 15-35.

3.6.2. CO stripping experiments

CO stripping voltammetry is often used for characterization of fuel cell catalyst since long time, because CO oxidation peak potential and shape of CO stripping peak are surface sensitive. This technique can be successfully used not only for the evaluation of catalyst activity, but also for an estimation of electrochemically active surface area. Usually, the CO oxidation onset potential is the potential at which the adsorbed CO molecules on the surface of the catalyst start oxidation due to the presence of oxygenated species (oxy-hydroxide) on the surface of the electrocatalyst and has been effectively used for the determination of activity of the fuel cell catalyst towards CO oxidation [122]. Lower the onset potential, higher the activity for CO oxidation and vice versa.

CO stripping experiments were conducted at three different temperatures (25 and 85 and 105 °C), in order to study the CO tolerance of Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C,

Pt/WC/C, PtW/C and Pt/C anodes. These experiments were performed using a Solartron 1285 potentiostat/galvanostat in the standard fuel cell hardware. During experiment the anode, used as working electrode, was either fed with Ar or CO (1000 ppm in Ar balance), while the cathode, used as both reference and counter electrode, was constantly fed with hydrogen. The CO was firstly adsorbed on the anode for 30 minutes at a constant potential of 100 mV for 25 °C and at 50 mV for 85 and 105 °C and finally the anode was flushed with Ar for another 30 minutes.

3.6.3. *Online mass spectrometry (OLMS)*

Online mass spectrometer is a fast, selective and sensitive tool to identify the fuel cell reaction products, in order to recognize the nature of reaction products and understand the reaction mechanism and subsequently find out the best fuel cell catalyst. In the mass spectrometer a fraction of gaseous molecules is converted into ions by bombarding them with low energy electrons, resulting in the formation of single and multiple charged positive ions. The number and types of ions produced are strongly dependent upon the energy of collisions electrons. As the electrons energy increases, the number of ions produced also increases. The maximum number of ions that can be produced is in the energy range of 50-150 eV, depending on the type of gas, afterward the increase in electron energy leads to a decrease of number of ions produced. In most cases electron energy in the range 70-100 eV is used, in order to ensure possible yields of ions and sensitivity. The resultant ions are then separated according to their mass to charge ratio and finally directed to the detector.

Online mass spectrometry analysis was conducted to observe the oxidation of the CO adsorbed on the electrocatalyst surface. A mass spectrometer (Pfeiffer Vacuum GSD 301 Omnistar, quadrupole QMS 200 Prisma, W filament 70 eV electron energy with SEM 1000 V common voltage) was connected to the single cell anode outlet by a capillary heated at 170 °C. In these experiments the anode was either fed with H₂ or H₂/100 ppm CO, whereas the cathode was constantly fed with O₂, while keeping the cell at the condition of open circuit potential. An analytical calibration curve, which was obtained with five different concentration of CO₂ in H₂, was used to calibrate the data corresponding to the conversion of CO₂ ionization current in to CO₂ contents.

3.6.4. Cyclic voltammetry (CV)

Cyclic voltammetry is the most important and effective electrochemical technique for the study of electroactive species and electrode surfaces. Cyclic voltammetry allows the potential of electrode to be scanned between two fixed values, where the potential of the working electrode is scanned linearly from an initial value to a fixed final potential value, where the direction of the scan is reversed. The potential is then scanned to the initial value, where the scan is again reversed. The resulting current is then plotted as a function of applied potential to obtain the cyclic voltammogram, which gives information about the reaction occurring on the electrode surface [123].

In this work in-situ cyclic voltammetry was applied to the single cell electrodes in the real fuel cell hardware to elucidate the surface properties of the electrodes. In these experiments the anode was used as the working electrode and cathode was used as the reference and counter electrodes. During experiment the anode was exposed to argon and the cathode was exposed to hydrogen. The gases used were humidified at atmospheric pressure. The anode potential was cycled between 0.1 and 0.7 V, at a scan rate of 50 mVs^{-1} , whereas the cathode potential was cycled between 0.1 and 1.2 V using the same scan rate. The cyclic voltammograms were obtained after cooling the cell down to room temperature.

3.6.5. Stability study

Two basic approaches are commonly used to assess the durability of fuel cell and its components: The steady state life time test and the accelerated stress test (AST). Certainly, the most reliable way to investigate the stability of the fuel cell is it to test the fuel cell in real steady state operating conditions. For example, Wang et al. [124] carried out the life time study of the fuel cell for 2250 h at a current density of 160 mAcm^{-2} . They observed an increase in particle size of Pt for both the anode and cathode using TEM after the life time test. Although, reliable information can be obtained about the degradation of fuel cell components under real life operating conditions, however this method is unfeasible for large scale applications, because it is time consuming and costly. Therefore, AST is becoming

popular among the fuel cell researchers, due to significant reduction in time of experiment for life time evaluation. AST can be applied either in-situ or ex-situ to whole cell or single component to evaluate the stability. During AST application, the fuel cell and its component experience the same conditions as they do experience under real operating conditions [125]. Several accelerated stressors are used for catalyst degradation including: Potential cycling from low to higher potential, square wave potential and steady state potential control at fixed voltage values [48].

In this work, potential cycling from low to higher potential was used to evaluate the stability of anode catalyst. The anode potential was scanned between 0.1 and 0.7 V, at a scan rate of 50 mVs^{-1} . The cycling was performed at room temperature, in increments of 1000 cycles up to a total of 5000 cycles. The performance of the MEAs was evaluated before and after each 1000 potential cycles, by measuring polarization curves and anode overpotentials due to the presence of CO (η_{CO}). This anode overpotential was calculated at each current density from the values of the cell potential in the absence (pure H_2) and presence ($\text{H}_2 + 100 \text{ ppm CO}$) of CO. Cyclic voltammetry was also applied to the cathode by the same procedure as for the anode, after the above-mentioned 5000 potential cycles.

CHAPTER III

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1. Effect of heat treatment on the activity and stability of carbon supported PtMo alloy electrocatalysts for hydrogen oxidation in the proton exchange membrane fuel cells.

4.1.1. Characterization of PtMo/C electrocatalysts

Temperature programmed reduction technique was used to study the reducibility and reduction temperature of oxide species, such as platinum and molybdenum oxides, dispersed on the carbon support. Figure 6 shows the TPR profile of the as-prepared PtMo/C catalyst, in which two hydrogen consumption peaks can be observed (at around 300 and 700 °C). The lower temperature reduction peak has normally been assigned to the reduction of MoO₃ [126,127],

whereas the higher temperature reduction peak has usually been attributed to the reduction of MoO₂,

Usually the reduction of these Mo species occurs at higher temperatures compared to Pt/MoO₃ and Pt/MoO₂, but due to the presence of Pt, in this case the hydrogen consumption peaks for Mo species are shifted to lower temperatures. This is due to the fact that the hydrogen molecule is first activated and dissociated into H atoms on Pt centers at a low temperature, which then enter into the lattice of these Mo species, occupying interstitial sites and behaving as intermediate in the reduction of these species to lower the activation energy. Consequently the reduction temperature is substantially decreased in the presence of Pt. On the basis of these hydrogen consumption peaks the catalyst samples were then heat treated

Figure 6: TPR profile of the as-prepared PtMo/C catalyst carried out by passing a mixture of Ar/H₂ (10 %) through a 16 mg sample with the designed temperature program: from 0 to 1000 °C at a heating rate of 10 °C/min.

under hydrogen atmosphere at various temperatures ranging from 400-700 °C during 1 h to reduce these surface Mo oxide species aiming to form a true alloy PtMo/C catalyst. The composition of the PtMo/C catalyst samples was determined by EDX. The average concentration of Pt and Mo in the as-prepared and thermally treated catalysts resulted in Pt:Mo atomic ratios of 64:36 and 59:41, respectively. A little difference between the atomic proportion of as-prepared and and heat-treated catalyst was observed, but this could be due to experimental error and is within the accuracy limit (95%) of EDX. The structure and phase analyses of the catalyst samples were performed by XRD. The XRD patterns obtained are shown in Figure 7. They have been recorded before and after heat treatments performed in the temperature range between 400 and 700 °C, and predominantly exhibit the peaks of the single-phase face-centered cubic (FCC) crystalline structure of Pt, corresponding to the (111), (200), (220), (311) and (222) planes. The diffraction peak located around $2\theta = 25^\circ$ corresponds to the (002) crystal plane of the hexagonal structure of the Vulcan XC-72R carbon support. Besides this peak, all patterns present only diffraction peaks associated to the Pt crystal structure, indicating the absence of any other segregated crystalline phase. No oxide phases of Mo have been detected, neither any dislocation of diffraction peaks was observed

when diffraction patterns of as-prepared PtMo/C and heat-treated at different temperature were compared with that of pure Pt/C catalyst. Therefore, it is inferred that Mo is not alloyed with Pt and may be present in amorphous structures.

The mean crystallite sizes were calculated from the separated and more symmetric (220) diffraction peak compared to other peaks, using the Scherrer equation. The effect of the heat treatment on the crystallite size of the catalysts is shown in Figure 8. As can be seen, the crystallite size of the catalyst increases as the heat treatment temperature increases, particularly above 500 °C. The crystallinity increased expectedly with the increasing temperature of heat treatment, as can be deduced from the sharpness and intensity of the diffraction peaks of the samples heat treated at different temperatures. Since heat treatment causes agglomeration of the metal particles which in turn increases their sizes. Smaller particles have less number of crystal planes compared to larger particles, therefore the diffraction peaks of smaller particles are broader than those of larger particles. Figure 9 shows typical TEM images of the as-prepared and heat-treated (600 °C) PtMo/C electrocatalysts, in which remarkably uniform and disperse alloy particles can be observed. Average particle diameters of 2.2 and 3.2 nm were determined from the TEM images, respectively. It is clear from the TEM image that the crystallinity increases after the heat treatment, as also evidenced by XRD. Regarding the as-prepared catalyst, the average particle diameter is similar to the mean crystallite size determined from the corresponding XRD pattern by means of the Scherrer equation (see Figure 7). This fact suggests that most of the particles are single crystals. In the case of the catalyst heat-treated at 600 °C, the average particle diameter (of 3.2 nm) obtained from the TEM images is noticeably lower than the mean crystallite size determined by XRD (around 15 nm, see Figure 8). Clearly, these last two values are not consistent, because the particles cannot be smaller than the crystals (a particle is made of several crystallites). Doubtlessly, the size distribution of the group of particles analyzed by TEM does not represent the particle size distribution of the whole sample, and there must be bigger particles compared to smaller particles not recorded in the TEM images. It is worth mentioning that the particle size distributions were determined from sets of several TEM pictures (not shown here). Then, for some reason, the big particles of the heat-treated catalyst were not included in the sample holder for TEM analysis, perhaps due to some effect induced by the sample preparation. However, the behavior of the average crystallite size as a function of the temperature of the heat treatment (shown in Figure 8) is very clear, and XRD results are more reliable than those of TEM, due to the larger statistic involved in the XRD analysis as

Figure 7: XRD patterns of PtMo/C samples recorded before and after heat-treatment at various temperatures.

compared with TEM. To further investigate the effect of the heat treatment on the Pt 5d band properties in the PtMo/C electrocatalysts, XANES spectra were recorded at the Pt L_3 edge. Figure 10 shows these spectra for both catalysts: the as-prepared PtMo/C and the heat-treated at 600 °C, polarized at 50 mV vs. RHE before and after CO adsorption. The X-ray absorption at the Pt L_3 edge corresponds to $2p_{3/2}$ -5d electronic transitions and the magnitude of the hump (the so-called white line) located at about 5 eV is directly related to the occupancy of 5d electronic states [45]. The lower the occupancy, the higher the magnitude of the white line. A very small but consistent increase in the white line intensity is observed in the XANES spectra of the heat-treated PtMo/C electrocatalyst as compared with that corresponding to the as-prepared catalyst, in the presence of both H_2 (Figure 10a) and H_2/CO (Figure 10b) atmospheres. This indicates that the occupancy of the Pt 5d band in the PtMo/C catalysts increases marginally with the heat treatment. Some works showed that the number of Pt d band vacancies depends on the changes of particle size induced by heat treatments, as also seen in the present case. Santos et al. [92] demonstrated that for a PtV/C alloy electrocatalyst, the occupancy of Pt 5d band practically remains the same when the temperature of heat treatment is increased from 300 to 850 °C. This was probably due to very small changes in particle size with the increase of heat treatment temperature. The effect of the particle size on the white line intensity of XANES spectra for Pt/C at various potential has been investigated previously [45].

Figure 8: Average crystallite size estimated from XRD patterns of the PtMo/C catalysts, before heat-treatment and after heat-treatment performed at various temperatures ranging from 400-700 °C.

Figure 9: TEM images and particle size distribution of as-prepared PtMo/C catalyst and the PtMo/C catalyst heat-treated at 600 °C.

Figure 10: XANES spectra of the Pt L₃ edge for the as-prepared PtMo/C catalyst (a and b), the PtMo/C catalyst heat-treated at 600 °C (a and b) and the commercial Pt/C catalyst (c); exposed to H₂ (a), H₂/CO (b) and both H₂ and H₂/CO (c).

A great increase in the magnitude of white line with the increase in the applied potential is observed for the catalyst of small particle size (1 nm) in comparison to large particle sized (3.7 nm) catalyst. This increase in white line intensity with increasing applied potential for the catalysts with two different particle sizes is associated with a modification of average Pt oxidation state and it has been discussed in detail by various authors [128,129]. Mukerjee et al. [24] observed a small increase in the Pt white line magnitude for PtMo/C when compared

with Pt/C, indicating an increase in the number of Pt 5d band vacancies in PtMo/C due to alloying. A similar phenomenon is observed here, as it can be seen from the comparison of results in Figure 10. In order to study the effect of CO adsorption on the electronic properties of Pt, XANES spectra were also recorded for the Pt/C catalysts before and after the CO adsorption, as shown in Figure 10c. In the case of Pt/C an increase in the white line intensity is clearly observed, when the catalyst is exposed to CO. This is due to the fact that the adsorbed CO causes an increase in the number of Pt 5d band vacancies, compared to hydrogen alone, which is a result of electron back-donation from Pt to CO. Similar but smaller effect is observed for the PtMo/C catalysts, as can be seen from the comparison of the spectra shown in Figure 10. The increase in white line intensity for PtMo/C compared to Pt/C has been discussed in section 4.2.1 in Figure 22.

4.1.2. Single cell performance of PtMo/C electrocatalysts

The performance and hydrogen oxidation activity of the PtMo/C electrocatalysts were evaluated by measuring the polarization curves both in the presence of pure H₂ and H₂ containing 100 ppm CO. Figure 11 shows the single cell polarization curves obtained for anodes supplied with pure H₂ and H₂ containing 100 ppm CO for the as-prepared PtMo/C electrocatalyst and the catalysts heat-treated at different temperatures, ranging from 400-700 °C. As can be seen, the PtMo/C electrocatalyst heat-treated at 600 °C, showed the highest hydrogen electro-oxidation activity in the presence of 100 ppm CO. This behavior may be related to the formation/stabilization of active Mo species for hydrogen oxidation in the presence of CO at 600 °C. Also, Han et al. [90] illustrated that the CO oxidation activity of Pt can be improved significantly by heat treatment. From here onward only the as-prepared PtMo/C catalyst and the heat-treated at 600 °C will be discussed. The polarization curves of these two catalysts, measured at several stages of the cycling process, supplied with both pure H₂ and H₂ containing 100 ppm CO are shown in Figure 12.

The corresponding anode overpotentials introduced by CO are shown in Figure 13. The performance of the MEA was evaluated before the cycling process and after each 1000 potential cycles, up to a total of 5000 cycles. As can be observed in Figure 12a, the performance declines significantly with the cycling process for the as prepared catalyst (either

if the anode is supplied with pure H₂ or H₂ containing 100 ppm CO). In addition to this performance degradation, an increase of the anode overpotential due to the CO poisoning is also observed, as shown in Figure 13a. However, the decline in the performance of the MEA prepared with the heat-treated catalyst is very small in both cases (with pure H₂, and with H₂

Figure 11: PEM single cell polarization curves measured at 85 °C. The Pt/C cathodes were supplied with O₂; and the anodes (PtMo/C heat-treated at different temperatures) were supplied with pure H₂ and H₂/100 ppm CO.

containing 100 ppm CO) even after 5000 cycles. Similarly, a small increase in anode overpotential was observed for this catalyst, as a result of the cycling process, as can be seen in Figure 13b. A comparison between the anode overpotential of both catalysts after each 1000 cycles, for a current density of 1 Acm⁻², is shown in Figure 14. A very small variation in the anode overpotential can be observed for the heat-treated catalyst as compared to the as-prepared catalyst. These results show that the degradation of the cell performance could be effectively controlled by a heat treatment applied to the catalyst. Although the active surface area of the catalyst is reduced by a growth of the particles, induced by the heat treatment, this growth of the particles may have a positive effect on the catalyst stability, as the very fine particles are unstable [91,130,131].

Figure 12: PEM single cell polarization curves measured at 85 °C after multi-cycling treatments. The Pt/C cathodes were supplied with O₂; and the anodes (the as-prepared PtMo/C (a) and the heat-treated at 600 °C (b)) were supplied with pure H₂ and H₂/100 ppm CO.

4.1.3. Cyclic voltammetry and stability study of PtMo/C electrocatalysts

Cyclic voltammetry was performed to elucidate the surface properties of the electrocatalysts. The cyclic voltammograms of both, the as-prepared PtMo/C and heat-treated electrocatalysts conducted in MEA arrangements are shown Figure 15. Besides the well-known hydrogen adsorption/desorption peaks located in the potential range of 0.15-0.35 V vs.

Figure 13: Anode overpotential curves (η_{CO}) measured prior the cycling process and after each 1000 potential cycles, up to a total of 5000 cycles, for the untreated PtMo/C catalyst (a) and the PtMo/C catalyst heat-treated at 600 °C (b).

RHE, a peak at about 0.45 V in the positive-going scan can be clearly seen for both electrocatalysts, while in the negative-going scan two weakly resolved peaks in the potential region between 0.2 V and 0.4 V vs. RHE can be observed. These peaks have generally been attributed to the reduction-oxidation of Mo, from Mo (IV) to Mo (VI) and vice versa. The present voltammetric results agree well with previously reported data [22,89,106]. The stability of both the as-prepared and the heat-treated PtMo/C catalysts was evaluated up to 5000 potential cycles, and the cyclic voltammograms shown in Figure 15 are those recorded after each 1000 potential cycles. A decrease in the current density was observed for both catalysts, as a consequence of the cycling process. However, for the as-prepared catalyst, the

decrease in the current density is proportional to the number of cycles, whereas for the heat-treated catalyst, the current density becomes practically constant after 2000 potential cycles. This fact explains the small variation in the anode overpotential observed for the heat-treated catalyst, in the polarization measurements. In both cases a decrease in the reduction-oxidation peaks of Mo is observed, which is an evidence that dissolution of Mo from the anode takes place. This is confirmed by the cyclic voltammograms of the Pt/C cathode shown in Figure 16, which were recorded after 5000 potential cycles of the anodes. The peak at 0.45 V, which is very characteristic of the presence of Mo species in the system, can be clearly observed.

Figure 14: Anode overpotential (η_{CO}) measured at 1 Acm⁻² prior the cycling process and after each 1000 potential cycles, for the untreated catalyst and the catalyst heat-treated at 600 °C.

This shows that something of Mo is dissolved from the anode, and passes through the electrolyte membrane to reach the cathode, but eventually some Mo ionic species remain stuck in the electrolyte membrane. In order to study the migration of these Mo species, scanning electron microscopy and X-ray analysis of both the new and cycled MEAs (with the as-prepared PtMo/C catalyst in the anode) were performed after the polarization measurements. Figures 17a and 17b present scanning electron micrographs of cross sections of the MEAs, recorded with backscattered electrons, before the cycling process and after 5000 cycles, respectively. The carbon cloth, anode and the cathode catalyst layers, and the membrane can be easily identified in the new and cycled MEAs. Some signs of deterioration can be appreciated in the cycled MEA, mainly related to structural and morphological features

Figure 15: Cyclic voltammograms of anodes composed of the untreated PtMo/C catalyst (a) and the PtMo/C catalyst heat-treated at 600 °C (b), after multiple cycles.

of their components. Figures 18a, 18b and 18c show X-ray spectra of the membrane, anode and cathode of both MEAs, recorded with a 20 keV incident electron beam and a wavelength dispersive spectrometer (WDS), in the energy range between 2.28 and 2.35 keV. These spectra were taken from the regions identified with white spots in Figure 17a and Figure 17b. As can be seen, the S-K α peak is present in all the spectra, which is due to the sulfur content of the Nafion®. The Mo-L α peak and Pt-M₃N_{4.5} peaks are also present in the spectra of the anodes, and Pt-M₃N_{4.5} peak is present in the spectra of cathodes which correspond to metal content of PtMo and Pt/C catalysts, respectively. The presence of these peaks in the mentioned spectra is to be expected. However, the presence of Mo in the cathode of cycled MEA is also detected, as manifested by the Mo-L α peak, indicated by an arrow in Figure 18c. This fact is in agreement with the results of the cyclic voltammetry performed to the Pt/C cathodes after 5000 potential cycles (see Figure 16). During cycling process, the Mo is

Figure 16: Cyclic voltammograms of the Pt/C cathodes measured after 5000 potential cycles of the untreated PtMo/C anode (a) and the anode heat-treated at 600 °C (b).

partially dissolved from anode, passes through the membrane, and reaches the cathode, as was previously mentioned. On the other hand, a small amount of Pt can be appreciated in the membranes, as manifested by the Pt-M₃N_{4.5} peak, indicated by an arrow in Figure 18a, but in this case, the presence of Pt could be due to a contamination produced by the transversal cut of the MEAs during the sample preparation, because the presence of Pt is detected in both MEAs. The significant decrease of the MEA performance indicates that the Mo species can interfere not only with the conduction of protons in the membrane, but also in the kinetics of

Figure 17: Scanning electron micrographs of cross sections of the new (a) and cycled (b) MEAs, recorded with backscattered electrons.

oxygen reduction reaction (ORR) when they reach the cathode side. There is scarce information in the literature about the stability of PtMo/C electrocatalysts. Lebedeva et al. [89] showed that PtMo/C catalysts prepared by formic acid and formaldehyde methods are unstable, and a gradual loss of Mo from the anode takes place due to its dissolution and its migration to the electrolyte. Long term stability measurements of PtMo/C catalysts under steady state condition at a cell voltage of 0.6 V were performed by Mukerjee et al. [88], which showed a very small variation in the performance up to 1500 h of operation. However, the Mo dissolution is one of the major causes of performance losses of these catalysts, which can be improved up to some extent by a heat treatment.

Figure 18: WDS spectra of the membranes (a), anodes (b) and cathodes (c) of both MEAs, acquired with a 20 keV incident electron beam, in the energy range between 2.28 and 2.35 keV, corresponding to the areas indicated with the white spots in the micrographs (a) and (b) of Figure 17.

4.2. Molybdenum carbide based electrocatalysts for CO tolerance in proton exchange membrane fuel cell anodes.

4.2.1. Physical Characterization of Electrocatalysts

The results of elemental analysis obtained by EDX are given in Table 2. The corresponding EDX spectra are shown in Figure 19. A molybdenum content of only 19 wt. % was obtained for the Mo₂C/C (30 wt. %) support. The measured Pt and PtMo loadings (for the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C electrocatalysts) resulted less than the target value of 20 wt. %. It should be noted that the total Mo content of the PtMo/Mo₂C/C catalyst has contributions from the carbide and from the bimetallic particles. A small reduction in the Mo content of Mo₂C/C was observed after the addition of Pt and PtMo, which could be due to a partial dissolution of Mo during the deposition process. Surface areas of Mo₂C/C support and Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C electrocatalysts, determined by BET gas adsorption isotherms, are included in Table 2. A decrease in the overall surface area was observed for Pt/Mo₂C/C and PtMo/Mo₂C/C, which may be due to blocking of the pores by Pt and PtMo nanoparticles.

Figure 20 presents the X-ray diffraction patterns obtained for Mo₂C/C, Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C electrocatalysts. The pattern of Mo₂C/C presents peaks of both α -Mo₂C and β -Mo₂C [132,133], whereas that of Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C predominantly exhibit the peaks of the crystalline structure of Pt. These results of XRD are consistent to the already reported data [133], where the Mo₂C peaks disappeared after the addition of Pt to the Mo₂C/CNTs support. It is worth mentioning that significant contents of molybdenum in the samples were detected by EDX, despite the fact that almost no molybdenum crystalline phases were detected by XRD. The average Pt crystallite sizes calculated for these catalysts are given in Table 2. The values of lattice parameters (Table 2) indicate no inclusion of Mo in the Pt crystallites. Figure 21 shows typical TEM images of the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C catalysts. The average particle diameters measured from these images are consistent with the mean crystallite sizes calculated from the XRD patterns, as can be seen in Table 2. A clear difference between the carbon black and molybdenum carbide supports can be observed from these TEM images. Quite uniform

Table 2: Chemical compositions, crystallite/particle sizes, lattice parameters and BET surface areas of the Mo₂C/C support and the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C electrocatalysts.

Electro-catalysts	Elements (wt%)			Pt crystallite/		Pt Lattice	BET surface
	determined by			particle size(nm)		constant (Å°)	area (m ² /g)
	EDS					XRD	
	Pt (%)	Mo (%)	C (%)	XRD	TEM		
Mo ₂ C/C	NA	19.0	81.0	NA	NA	NA	113
Pt/Mo ₂ C/C	16.1	12.1	71.8	3.0	2.5	0.392	85
PtMo/Mo ₂ C/C	15.0	14.5	70.5	2.5	2.4	0.392	88
PtMo/C	13.3	3.0	83.7	2.4	2.5	0.391	190

Figure 19: EDS patterns of Mo₂C/C, Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C electrocatalysts.

dispersion of Pt and PtMo particles was obtained for all catalysts. The effect of Mo₂C and Mo on the occupancy of d electronic states in Pt atoms of the catalysts was investigated by measuring XANES spectra at the Pt L₃ edge. The X-ray absorption at the Pt L₃ edge corresponds to 2p_{3/2}-5d electronic transitions and the magnitude of the white line is directly related to the occupancy of 5d electronic states. Differences in XANES spectra or in white line intensities are mainly related to differences in the electronic properties (the oxidation state) of the absorbing atom due to the electron donating or withdrawing properties of the neighboring atoms. An increase in white line intensity indicates an increase in the number of vacancies.

Figure 22 shows XANES spectra of the PtMo/Mo₂C/C, PtMo/C and Pt/C electrocatalysts, recorded at the Pt L₃ edge before and after the adsorption of CO with the electrodes polarized at 50 mV vs. RHE. A slight but consistent increase in the white line intensity of PtMo/Mo₂C/C and PtMo/C as compared to Pt/C, can be observed in the XANES spectra recorded in H₂ atmosphere (see the inset of Figure 22a). This indicates that the presence of Mo or Mo₂C near the Pt atom may induce a slight increase in the number of Pt 5d band vacancies by changing its chemical environment. Figure 22b shows the XANES spectra recorded after the CO poisoning of the catalysts. As it can be seen, a noticeable increase of the white line intensities was produced by the CO adsorption in three electrocatalysts, as a result of electron back donation from Pt to CO (see the inset of Figure 22b). Because the white line intensity of Pt/C is smaller than those of PtMo/Mo₂C/C and PtMo/C in the absence of CO, but the three white line intensities are similar in the presence of CO, the change caused by CO adsorption is greater for Pt/C than for PtMo/Mo₂C/C and PtMo/C catalysts, implying that more electrons are transferred from Pt to CO in the case of Pt/C. For Pt/C and PtMo/C electrocatalysts, the present results are in agreement with previously reported data [22,105]. The higher white line intensity of PtMo/C and PtMo/Mo₂C/C compared to Pt/C has been attributed to the presence Mo oxides or carbide species near Pt atoms, which induces an electron withdrawing effect and thus decrease the Pt-CO adsorption energy. This in turn leads to the greater CO tolerance of Mo based electrocatalysts.

Figure 20: X-ray diffraction patterns of the Mo₂C/C support and the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C electrocatalysts.

Figure 21: TEM images of the Pt/Mo₂C/C, PtMo/Mo₂C/C, and PtMo/C electrocatalysts.

4.2.2. Electrochemical characterization of the electrocatalysts

Figures 23 and 24 show polarization and power density curves obtained for the Pt/C, Pt/Mo₂C/C, PtMo/C and PtMo/Mo₂C/C anodes, supplied with pure H₂ and H₂ containing 100

ppm CO, using Pt/C cathodes, supplied with O₂. These curves were recorded before the cycling process and after 1000, 3000 and 5000 potential cycles. As can be seen in Figs. 23b and 24a, Pt/Mo₂C/C and PtMo/Mo₂C/C showed the highest initial (0 cycle) hydrogen oxidation activity in the presence of CO, giving CO induced overpotentials (η_{CO}) of ca. 120 mV for 1Acm⁻² of current density, as compared to overpotential of 150 mV for PtMo/C, shown in Fig. 24b. On the other hand, for the Pt/C catalyst, the effect of CO poisoning is so

Figure 22: XANES spectra at the Pt L₃ edge for the Pt/C, PtMo/C and PtMo/Mo₂C/C electrocatalysts exposed to H₂ (a) and H₂/CO (b) atmospheres.

Figure 23: PEM single cell polarization and power density curves measured at 85 °C with freshly prepared electrodes, and after 1000, 3000 and 5000 potential cycles. The Pt/C (a and c) and Pt/Mo₂C/C (b and d) anodes were supplied with pure H₂ and H₂/100 ppm CO and the Pt/C cathodes were supplied with O₂.

adverse that the current density does not reach 1 Acm⁻² (see Figure 23a). For Pt/C, a similar behavior can be observed in the power density curves, where the power density didn't reach 200 mWcm⁻² when the anode fuel is H₂ containing 100 ppm of CO (see Figure 23c). On the other hand, the Pt/Mo₂C/C catalyst yielded a power density of 400 mWcm⁻² in the presence of H₂/100 ppm CO, as shown in Figure 23d. For the PtMo-based catalysts (Figures 24c and 24d) high power densities were obtained for PtMo/C in the presence of both H₂ and H₂/100 ppm CO, but the decay of performance due to the cycling is much higher for PtMo/C than for PtMo/Mo₂C/C. The improved CO tolerance of the carbide-based electrocatalysts may be related to the efficiency of Mo₂C/C to desorb or oxidize the adsorbed CO through a WGSR [71,77,134]. As explained before (see reaction 7), in such type of reaction the water adsorbed on the surface of the electrocatalysts is responsible for the oxidation of CO present in the

anode stream. It has been shown previously [44] that no WGSR occurred when the anode was fueled with dry gas, suggesting that in the absence of water no such reaction take place. The WGSR has been observed through the OLMS.

After an initial decrease in the cell voltage, a quite constant cell performance was observed after around 1000 cycles, both in the presence and absence of CO, by the Pt/Mo₂C/C and PtMo/Mo₂C/C electrocatalysts (see Figures 23b, and 24a). On the other hand for PtMo/C, the MEA performance in the presence of H₂ or H₂ containing CO deteriorates continuously with the cycling process, as can be observed in Figure 24b. This can be due to a greater dissolution of Mo from the PtMo/C anode and its migration through the electrolyte membrane towards the cathode. When the catalyst support is molybdenum carbide, not only there is an increase in the oxidation of adsorbed CO, but also the electrocatalysts are more stable, as can be deduced from the polarization measurements. Results for the Pt/C anode show a stable performance of the MEA up to 5000 potential cycles in the presence of both H₂ and H₂/100 ppm CO, as can be observed in Figure 23a, which is in agreement with previous results, where a better stability was obtained for the Pt electrocatalysts in comparison with Pt-M (M=second metal) electrocatalysts in PEMFCs [50].

Figure 25 shows a comparison between the anode overpotentials of the electrocatalysts, before the cycling process and after each 1000 cycles, for a current density of 1 Acm⁻². A very little variation in the anode overpotential of Pt/Mo₂C/C can be observed, reaching an almost constant value after 1000 cycles, whereas, the overpotentials of PtMo/Mo₂C/C increase in the first 2000/3000 cycles and then decrease, reaching fairly constant values after 4000 cycles. On the other hand the overpotentials of PtMo/C remain variable during all the cycling process. The results of anodic overpotentials show that the cell performance can be significantly improved by using Pt or PtMo supported on Mo₂C/C as anode electrocatalysts, instead of using PtMo supported on carbon, as it is suggested by the values of overpotentials obtained after 4000/5000 cycles.

Figure 24: PEM single cell polarization and power density curves measured at 85 °C with freshly prepared electrodes, and after 1000, 3000 and 5000 potential cycles. The PtMo/Mo₂C/C (a and c) and PtMo/C (b and d) anodes were supplied with pure H₂ and H₂/100 ppm CO.

Figure 25: Anode overpotential (η_{CO}) measured at 1 Acm⁻² prior the cycling process and after each 1000 potential cycles, for the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C catalysts.

Figure 26 shows the CO stripping profiles of Pt/Mo₂C/C, PtMo/Mo₂C/C, PtMo/C and Pt/C electrocatalysts, measured at 25 and 85 °C. At 25 °C, the profiles of Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C exhibit CO electrooxidation peaks at about the same potential (0.665 V), meaning that at room temperature these three electrocatalysts have practically the same ability to oxidize the CO. For the Pt/C catalyst the CO electrooxidation occurs at a higher potential, indicating a poorer CO tolerance as compared to the other electrocatalysts, as also evidenced by polarization measurements. For the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C catalysts, part of CO is adsorbed on the Pt surface and part is directly oxidized to CO₂ (see Figure 27) whereas for Pt/C catalyst, the only process is the adsorption on the catalyst surface. This explains why the CO stripping currents are larger for the Pt/C catalyst. These results are in agreement with previously reported data [30], where the CO oxidation shows a shift of 65 mV vs RHE towards more negative potentials for Pt/MoC/C in comparison to Pt/C. An increase in the temperature induces a decrease in the CO oxidation potential of the two carbide-based electrocatalysts, therefore at higher temperatures the molybdenum carbide-based electrocatalysts are more effective for the CO oxidation than the PtMo/C electrocatalyst. Figure 27 shows the results of OLMS, obtained with the anodes maintained at the condition of open circuit potential. It can be observed that CO₂ production takes place when the anode is fed with H₂/100 ppm CO for the three catalysts, which evidences the oxidation of CO through a WGSR on the surface of the electrocatalysts [135]. There are some differences in the extent of the CO₂ production, but this could be due to oscillations of the spectrometer response.

Figure 26: CO stripping curves for the anodes formed by Pt/Mo₂C/C, PtMo/Mo₂C/C, PtMo/C and Pt/C electrocatalysts, measured at 25 °C (above) and 85 °C (below).

Figure 27: Ion current obtained by OLMS with $m/z = 44$ for the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C anodes supplied with pure H₂ or H₂/100 ppm CO. Cathodes formed by Pt/C were supplied with O₂.

4.2.3. Degradation of the electrocatalysts

Figures 28 and 29 show the cyclic voltammograms of the Pt/C, Pt/Mo₂C/C, PtMo/C and PtMo/Mo₂C/C electrocatalysts, measured before the cycling process and after 1000, 3000 and 5000 cycles. Besides the Pt-H desorption and adsorption peaks, an oxidation peak can be observed at ca. 0.45 V vs. RHE in the positive-going scan, for all the catalysts except Pt/C,

and a relatively broad peak can be seen at 0.42 V vs. RHE in the negative-going scan, in the voltammetric profiles of the Mo-based electrocatalysts. This redox couple is in agreement with data from the literature and corresponds to an oxidation/reduction couple of Mo^{+4} into Mo^{+6} [22,39,105].

In all electrocatalysts except Pt/C a decrease in the peaks related to the oxidation/reduction reactions of Mo is noticeable after the potential cycling, which suggests that a partial dissolution of Mo species takes place in the acidic environment of the cell [46,89]. Nevertheless, for Pt/Mo₂C/C (Figure 28b) and PtMo/Mo₂C/C (Figure 29b) electrocatalysts the current densities and peak positions practically remain constant after 1000 potential cycles, suggesting that after an initial dissolution of some Mo species, no further dissolution takes place. On the other hand, the PtMo/C (Fig. 29a) suffers a gradual decrease in

Figure 28: Cyclic voltammograms of the anodes composed of Pt/C (a) and Pt/Mo₂C/C (b), measured before the cycling process and after 1000, 3000 and 5000 potential cycles.

the current density and peak position during all the cycling process. This indicates that in spite of dissolution of some Mo species from $\text{Mo}_2\text{C}/\text{C}$ support in $\text{PtMo}/\text{Mo}_2\text{C}/\text{C}$, the total dissolution of Mo is lower in $\text{PtMo}/\text{Mo}_2\text{C}/\text{C}$ than in PtMo/C . These results are in agreement with the polarization measurements, where smaller variations in the anode overpotentials were observed for the $\text{Pt}/\text{Mo}_2\text{C}/\text{C}$ and $\text{PtMo}/\text{Mo}_2\text{C}/\text{C}$ electrocatalysts. Thus, the molybdenum carbide not only attenuates the CO poisoning, but also provides stability to the electrocatalysts, through the stabilization of the metal nanoparticles.

The dissolution of Mo species from the anode electrocatalysts and their migration towards the Pt/C cathodes were confirmed by cyclic voltammetry applied to the single cell cathodes, which was conducted initially after polarization measurements and then after 5000 potential cycles of the anode. As depicted in Figure 30, a peak at 0.45 V vs. RHE in the positive-going scan can be observed in all the voltammograms, (except for the cell with the

Figure 29: Cyclic voltammograms of the anodes composed of PtMo/C (a) and $\text{PtMo}/\text{Mo}_2\text{C}/\text{C}$ (b) measured before the cycling process and after 1000, 3000, 5000 potential cycles.

Pt/C anodic catalyst, Figure 30a), i.e located at the same potential as in the voltammetric profile of the anode. This evidences the migration of Mo from the anode to the cathode, through the electrolyte membrane. Initially the intensities of Mo peaks in the Pt/C cathodes are weaker than those in the Pt/Mo₂C/C, PtMo/Mo₂C/C and PtMo/C anodes, but the corresponding peaks became sharper with the cycling process. Finally, in all cases, the intensities of Mo peaks in the anode and cathode voltammograms became similar after 5000 potential cycles, even though these intensities were different for the different catalysts.

Scanning electron microscopy and X-ray analysis were performed in cross sections of new and cycled MEAs, in order to further investigate the migration of Mo species. As an example, Figures 31a and 32b show micrographs of the MEA composed by PtMo/Mo₂C/C in the anode and Pt/C in the cathode, recorded with backscattered electrons, before and after the cycling process, respectively. All the components of the MEA, such as the carbon cloth, the

Figure 30: Cyclic voltammograms of the Pt/C cathodes measured initially after polarization measurements and then after 5000 potential cycles of the Pt/C (a) Pt/Mo₂C/C (b), PtMo/C (c) and PtMo/ Mo₂C/C (d) anodes.

gas-diffusion electrodes and the electrolyte membrane, can be easily identified in these micrographs. Some signs of deterioration can be appreciated in the cycled MEA (Figure 31b), such as the presence of fractures in the gas-diffusion electrodes and detachments from the membrane. Similar features were observed in the micrographs of the other MEAs. The brightness of the catalyst layers is due to the presence of metal nanoparticles.

Figure 31: Scanning electron micrographs of cross sections of the MEA composed of PtMo/Mo₂C/C in the anode and Pt/C in the cathode, recorded before (a) and after (b) the cycling process.

Figure 32 shows X-ray spectra of the Pt/C cathodes of the MEAs composed by PtMo/Mo₂C/C and PtMo/C in the anode, recorded before and after the cycling process, with a 20 keV incident electron beam and a wavelength dispersive spectrometer, in the energy range between 2.28 and 2.35 keV. As it can be seen, the S-K $\alpha_{1,2}$ and S-K $\alpha_{3,4}$ peaks are present in all the spectra, which is due to the sulfur content of the Nafion®. The Pt-M γ peak is also present in all the spectra, which is due the platinum content of the Pt/C cathode catalysts. The presence of these peaks in the spectra is to be expected. Regarding the molybdenum, it was detected only in the cathodes of the cycled MEAs, as manifested by the Mo-L $\alpha_{1,2}$ peak. This fact is in agreement with the results of the cyclic voltammetry performed to the Pt/C cathodes. During the cycling process, the Mo is partially dissolved from the anode, passes through the membrane, and reaches the cathode, as it was previously discussed. It is worth mentioning that, a small amount of Mo can also be appreciated in the cathodes of the new MEAs, but in these cases, the presence of Mo is due to a contamination produced by the transversal cut of the MEAs during the sample preparation.

The molybdenum species that reach the cathode, interfere not only with the kinetics of oxygen reduction reaction (ORR) in the cathode, but also with the conduction of protons through the electrolyte membrane. Therefore the ORR, which itself is a kinetically slow process, is further slowed down by the presence of Mo ionic species, thus having a negative effect on the MEA performance. However, as seen previously, the use of molybdenum carbide support for the anode electrocatalyst can effectively control the loss of Mo species, helping to keep the CO tolerance. The molybdenum carbide not only provides stability, but also enhances the CO tolerance of the anode electrocatalyst, because of the exceptional thermal and chemical stabilities and good tolerance to poisons like CO. Thus, it was observed that the partially carburized Pt/Mo₂C/C and PtMo/Mo₂C/C electrocatalysts, resulted in a higher activity for the hydrogen oxidation reaction in the presence of 100 ppm of carbon monoxide, as compared to PtMo/C. In addition, degradation analyses showed that the carbide-based electrocatalysts are significantly more stable than PtMo/C.

Figure 32: WDS spectra of the Pt/C cathodes of new and cycled MEAs composed of PtMo/Mo₂C/C and PtMo/C in the anodes.

4.3. Pt modified tungsten carbide as anode electrocatalyst for hydrogen oxidation in proton exchange membrane fuel cell: CO tolerance and Stability

4.3.1. Physical Characterization of the Electrocatalysts

The wt. % of the different components of the catalysts as obtained by EDX are given in Table 3. The tungsten contents in the tungsten carbide supports are less than the target values of 10, 20 and 30 wt. % and this was also observed for the Pt loading of the Pt/WC/C, whereas the wt. % of PtW/C is very close to the desired value. Pt:W atom ratio is quite similar to the expected (3:2). The XRD results of the prepared materials are presented in Figure 33.

Table 3: Chemical compositions, crystallite/particle sizes and molar ratio of WC/C supports and the Pt/WC/C20 and PtW/C electrocatalysts.

Electrocatalysts	Element (wt%) determined by EDX			Pt crystallite/Particle size(nm)			EDX molar ratio
	Pt (%)	W (%)	C (%)	XRD	TEM	TEM after testing	
WC/C10	NA	8.7	91.3	NA	NA	NA	NA
WC/C20	NA	15.0	85.0	NA	NA	NA	NA
WC/C30	NA	19.3	80.7	NA	NA	NA	NA
Pt/WC/C20	16.9	12.5	70.6	2.4	3.6	3.6	NA
PtW/C	11.8	7.2	81.0	2.3	2.3	2.6	3.2:1.8

The XRD patterns of WC/C supports corresponds to simple hexagonal planes of WC according to JCPDF 65-8828. As can be observed, the intensities of peaks in the XRD patterns of tungsten carbide supports increases in the order of WC/C10 < WC/C20 < WC/C30, which are consistent to EDX analysis, where the percentage of W in the supports increases in the same order as mentioned above. The peak at ca. 25° corresponds to 002 crystal plane of hexagonal structure of Vulcan XC-72 carbon, which confirmed the existence of tungsten carbide supported on carbon. From the intensities of carbon peaks in these XRD patterns, it is confirmed that the WC/C10 contains highest amount of carbon, whereas the WC/C30 contains least amount of carbon, as also determined by EDX. The diffraction

patterns of Pt/WC/C10, Pt/WC/C20, Pt/WC/C30 and PtW/C exhibit major peaks of face centered cubic crystalline structure of Pt, corresponding to 111, 200, 220 and 311 crystal planes, besides weaker reflections of WC at 32°, 36° and 48° in the XRD pattern of Pt/WC/C20 and Pt/WC/C30. For Pt/WC10 the WC peaks didn't appear because of small

Figure 33: X-ray diffraction patterns of WC/C supports and Pt/WC/C10, Pt/WC/C20, Pt/WC/C30 and PtW/C electrocatalysts.

amount of W present. No shift in the positions of X-ray diffraction peaks of PtW/C was observed, when its XRD pattern was compared with that of pure Pt/C. It means that W is not alloyed with Pt in the PtW/C catalyst. In order to confirm this, XPS analysis of this catalyst was performed. Figure 34 shows the XPS spectra for the PtW/C catalyst in the Pt 4f and W 4f regions. As can be observed in Figure 34a, three pairs of doublets are found in the Pt 4f regions, which can be assigned to Pt (0), PtO (II) and PtO₂ (IV) species. The binding energy of these species are located at 71.24, 74.54 eV; 72.06, 75.36 eV and 73.48, 76.78 eV. The binding energies corresponding to first set of doublet (Pt 4f_{7/2} and Pt 4f_{5/2} of Pt (0)) are exactly the same as of pure Pt nanoparticles. This means that W is not alloyed with Pt in PtW/C catalyst, as also evidenced by XRD analysis. Figure 34b shows the XPS spectra in the W 4f region, where the first doublet at 35.67 and 37.82 eV can be assigned to WO₃ and the

Figure 34: XPS spectra of PtW/C catalyst. (a) Pt 4f region and (b) W 4f region

second doublet at 35.01 and 37.19 can be attributed to WO_2 . This indicates that W in the PtW/C is mostly present in the oxides form.

TEM images of Pt/WC/C20 and PtW/C shown in Figure 35, exhibit quite uniform dispersion of Pt and PtW particles. The Pt particles supported on WC/C are more evenly distributed than the PtW on carbon black, which suggests that the carbide phase facilitates the dispersion of particles. In the insets of Figure 35 are shown the histograms for both the catalysts, which are based on the analysis and counting of 200 particles from several different

regions of the same catalyst. As can be observed from the two histograms, the particle size distribution is quite uniform for both the catalysts. Results of crystalline sizes obtained from XRD and mean particle sizes obtained by TEM are included in Table 3. The particle size of PtW in PtW/C catalyst is compatible with the particle size of Pt in Pt/WC/C20 catalyst. Smaller the particle size, greater is the ESA and hence better is the catalytic activity.

Figure 35: TEM images of Pt/WC/C20 and PtW/C electrocatalysts.

4.3.2. Electrochemical results

Figure 36 shows the polarization curves obtained for the single cell with anodes (Pt/WC/C10, Pt/WC/C20 and Pt/WC/C30) supplied with H_2 and H_2 containing 100 ppm CO, and cathodes (Pt/C), supplied with O_2 . These polarization curves were recorded initially with freshly prepared electrodes and then after 1000, 3000 and 5000 potential cycles. As expected, the cell performance drops significantly when the H_2 containing CO is introduced to the anode. The highest initial (0 cycle) hydrogen oxidation activity in the presence of CO is observed for Pt/WC/C10 (Figure 36a) which gave CO induced overpotential (η_{CO}) of 288 mV for $1Acm^{-2}$ of current density as compared to overpotentials of 364 and 378 mV for Pt/WC/C20 (Figure 36b) and Pt/WC/C30 (Figure 36c). Nevertheless, for PtWC/C10 the cell voltage dropped more drastically with the cycling process, in the presence of both H_2 and H_2 containing CO, which is also confirmed by greater decrease of the current density in the

Figure 36: PEM single cell polarization curves measured at 85 °C. The anodes Pt/WC/C10 (a), Pt/WC/C20 (b) and Pt/WC/C30 (c) were supplied with pure H₂ and H₂/100 ppm CO and the Pt/C cathodes were supplied with O₂.

cyclic voltammograms with the cycling process for this catalyst, shown in Figure 37. This is an evidence that an increase in the amount of carbide, imparting stability to the catalyst. The results for Pt/C were presented before (see Figure 23a), where a constant cell performance in the presence of both H₂ and H₂ containing 100 ppm of CO were obtained. As Pt/WC/C20 showed a good stability and intermediate CO tolerance, further study was continued only with this catalyst and compared to PtW/C.

Figure 37: Cyclic voltammograms of anodes composed of Pt/WC/C10 (a) Pt/WC/C20 (b) and Pt/WC/C30 (c) catalysts, measured after initial polarization measurement, after 1000, 3000 and 5000 voltage cycles.

Figure 38 shows a comparison of the cell voltages for the Pt/WC/C20, PtW/C and Pt/C electrocatalysts in the presence and absence of CO, at two different temperatures. At 85 °C (Fig. 38a) better cell performance in the presence of CO is observed for Pt/WC/C20, which showed a CO induced overpotential (η_{CO}) of ca. 364 mV for 1 Acm^{-2} of current density, as

Figure 38: PEM single cell polarization curves measured at 85 °C (a) and 105 °C (b). The Pt/WC/C20 PtW/C and Pt/C anodes were supplied with pure H₂ and H₂/100 ppm CO and the Pt/C cathodes were supplied with O₂.

compared to overpotential of ca. 398 mV for the PtW/C catalyst. On the other hand for Pt/C the effect of CO poisoning is so severe that the current density hardly reached 1 Acm⁻². Such a high overpotentials can't be tolerated in the fuel cell operating practically. At higher temperature (105 °C) also, the Pt/WC/C20 showed a better CO tolerance in comparison to PtW/C. The anode overpotentials obtained were 104 and 174 mV at 1 Acm⁻² of current density for Pt/WC/C20 and PtW/C, respectively. Here the CO tolerance of Pt/C is comparable to that of PtW/C, showing the impact of increase in temperature on the CO tolerance. The CO tolerance mechanism of Pt-W catalysts has been studied in detail in literature [28,136]. It has been proposed that enhanced CO tolerance of these materials compared to Pt alone is due to the change in the oxidation state of W, occurring at low electrode potential which renders the

tungsten sites to be active for the dissociative adsorption of water and thus to the oxidation of adsorbed CO on Pt. Nevertheless, in the case of Pt/WC/C20 there may have also a contribution towards CO oxidation by the carbide phase. It has been investigated that the bonding between CO and tungsten carbides is much weaker than the bonding between CO and Pt, thus rendering the tungsten carbide catalyst sufficient immunity against CO poisoning [137]. Furthermore, it has been shown that WC can easily activate water to form surface hydroxyl [138]. The oxidation of adsorbed CO on Pt surface in the presence of WC proceeds through the following reaction [29].

Bernett et al. [139] has reported that WC alone is immune to CO poisoning in the presence of H₂, although the effect is not as efficient for Pt/WC. However, the CO poisoning of Pt cannot be avoided completely, because of its participation in reaction along with WC.

Further insights into these issues were possible from online mass spectrometry (OLMS) measurements with CO₂ detection, while keeping the cell under the condition of open circuit potential at two different temperatures. Figure 39 shows plots of the anode overpotential and the CO₂ production as a function of current density at two different cell temperatures, for Pt/WC/C20, PtW/C and Pt/C catalysts. These results clearly confirm that the increase of the cell temperature enhances the anode performance with H₂ containing 100 ppm of CO, for the all catalysts. It can be clearly observed from Figure 39 that the CO₂ production increases distinctively with the increase in temperature for both the catalysts, however in the case of PtW/C and Pt/C, the CO₂ production is much lower than for Pt/WC/C at the two temperatures, explaining the better CO tolerance of the carbide based catalyst as compared to the bimetallic and pure Pt catalysts. One more observation deduced from Figure 39 is that, as the anode overpotential decreases, generally CO₂ production increases and vice versa.

Figure 40 shows the results of OLMS experiments in which the cell was kept at open circuit and the anode was first fueled with pure H₂ and then switched to H₂/100 ppm CO, repeating the process several times, while the cathode was constantly fed with O₂. It can be observed that at 85 °C (see Figure 40a), CO₂ production is almost zero when the anode is fed with H₂/100 ppm CO for both the electrocatalysts. When the temperature is increased to 105 °C, as shown in Figure 40b, CO₂ production occurs when Pt/WC/C20 electrocatalyst is exposed to H₂/CO, which clearly indicates the occurrence of chemical CO oxidation on the

surface of electrocatalyst through the WGSR, whereas for PtW/C no oxidation takes place. Thus these results are consistent with the polarization curves, which showed a greater CO tolerance for Pt/WC/C20 anode.

Figure 39: Anode overpotential due to the presence of CO (η_{CO}) vs. current density (a) and CO₂ production vs. current density obtained by OLMS (b) plots for single cell with the anodes formed by Pt/WC/C20, PtW/C and Pt/C catalysts at 85 and 105 °C.

In order to evaluate the surface properties, cyclic voltammetry of anode electrocatalysts was conducted at room temperature and the results are shown in Figure 41. All the cyclic voltammograms show the typical Pt features for the underpotential (UPD) adsorption/desorption of hydrogen (0.05 to 0.35 V vs RHE). Beyond the UPD region the peaks observed in the 0.35-0.45 V vs. RHE range are mainly related to the redox processes

involving tungsten [23,28]. However, the double layer region in PtW/C, is broader than in Pt/WC/C, probably due to the presence of tungsten oxygenated species [23].

Figure 40: Ion current with $m/z=44$ detection obtained by OLMS for the Pt/WC/C20 and PtW/C anodes, supplied with H_2 or $H_2/100$ ppm CO. Cathodes formed by Pt/C and supplied with O_2 .

Figure 41: Cyclic voltammograms of Pt/WC/C20, PtW/C and Pt/C anodes.

The CO stripping profiles together with the CO₂ mass signal detected by OLMS are shown in Figure 42 for three catalysts at different temperatures. Results show that, an increase in temperature induces a decrease of the CO oxidation potential and the CO coverage for three catalysts. As shown before, this reduction of the CO coverage is responsible for the increase of the current densities with the increase of temperature (see Figure 39). For the Pt/WC/C20 the CO oxidation occurs at lower potentials at all temperatures as compared to PtW/C and Pt/C, which is in agreement with a relatively greater CO tolerance of the carbide based electrocatalyst. Thus the better CO tolerance of Pt/WC/C20 as compared to PtW/C was not only shown by polarization curves and online mass spectrometry experiments, but also by CO stripping experiments. The CO stripping potentials for Pt/C occur at almost the same values as for PtW/C, which are consistent to polarization curves where nearly the same CO tolerance was shown by Pt/C to PW/C, particularly at higher temperature.

Figure 42: CO stripping curves (a) and CO₂ production measured by OLMS (b) for the anodes formed by Pt/WC/C20 and PtW/C electrocatalysts at 25, 85 and 105 °C.

Figure 43: PEM single cell polarization curves measured with freshly prepared electrodes, after 1000, 3000 and 5000 potential cycles. The Pt/WC/C20 and PtW/C anode was supplied with pure H₂ and H₂/100 ppm CO and the Pt/C cathodes were supplied with O₂.

4.3.3. Stability of the electrocatalysts

Figure 43 shows the polarization curves for the Pt/WC/C20 and PtW/C catalysts, which were recorded initially with freshly prepared electrodes and then at various stages of the cycling process. While the cell voltage remains practically constant in the presence of H₂ and decreases slightly in the presence of H₂/CO for the Pt/WC/C20 (Fig. 43a), for the PtW/C a continuous decrease in cell voltage is observed in the presence of H₂ as well as H₂ containing 100 ppm of CO (Figure 43b). The corresponding anode overpotentials due to presence of CO were calculated for both the electrocatalysts and are shown in Figure 44. As

Figure 44: Anode overpotential (η_{CO}) measured prior the cycling process after 1000, 3000 and 5000 potential cycles, for the Pt/WC/C20 and PtW/C anode catalysts.

can be observed, the anode overpotentials increases continuously for the PtW/C catalyst, as a consequence of cycling process, whereas for Pt/WC/C20 the overpotentials increased only after 3000 potential cycles. These results show that Pt/WC/C20 seems to be more stable than PtW/C when operating in the PEM single cell anode. In order to further compare the stability of both electrocatalysts, cyclic voltammograms were recorded initially after the first polarization measurements and then after 1000, 3000 and 5000 cycles, as shown in Figure 45. A constant behavior is observed for Pt/WC/C20, for which a constant current density and fix positions of the oxidation/reduction peaks is noted. On the other hand for the PtW/C, the current densities and peak position vary with the cycle number and in addition, the double layer thickness also increases for this catalyst, indicating the formation of surface oxides. In this way, a higher stability of the Pt/WC/C20 electrocatalysts is not only shown by polarization

curves and anode overpotentials values, but also by the cyclic voltammograms of the anodes. The little greater stability of Pt/WC/C electrocatalyst is most probably due its carbide phase which is more corrosion resistant and stable in acidic solution, as compared to the carbon present in the bimetallic PtW/C electrocatalyst, as shown by the appearance of WO_3 peaks in XRD pattern (see Figure 46) of the PtW/C catalysts after testing in the fuel cell, whereas in the case of Pt/WC/C20 no such peaks appeared. It has been reported that WO_3 reacts with H_2 to produce hydrogen tungsten bronze (H_xWO_3), which is soluble in water [140]. Thus the degradation in performance is most likely due to the formation of these oxide species which leads to the slow formation of hydrogen tungsten bronze and finally to the detachment of Pt particles from the surface of the electrocatalysts after dissolution of the bronze. Similar results have been reported previously [141]. The effect of potential cycling on the particle size of the electrocatalysts was investigated by TEM and the results obtained are shown in Figure 47. As can be seen from the values given in the Table 3, the particle size of Pt/WC/C20 catalyst

Figure 45: Cyclic voltammograms of anodes composed of Pt/WC/C20 (a) PtW/C (b), measured after initial polarization measurement, after 1000, 3000 and 5000 voltage cycles.

Figure 46: XRD patterns of Pt/WC/C20 and PtW/C catalysts after testing.

practically remains constant after testing in the fuel cell, although a small agglomeration of particles was observed for this catalyst. On the other hand a small increase in the particle size was observed for the PtW/C, as shown in Table 3. Thus here also, a greater stability was shown by the Pt/WC/C20 as compared to PtW/C catalyst. The extent of W dissolution from the anode electrocatalysts was confirmed by the cyclic voltammetry of Pt/C cathodes after 5000 potential, as shown in Figure 48. The peaks present in the potential range of 0.35-0.45 V vs. RHE, are exactly the same as in the voltammetric profiles of anodes. Thus, it is certain that the W dissolved from the anode, travelled through the electrolyte membrane and reached the cathode. This crossover of the W species is the main factor responsible for the decline in the CO tolerance of single cell anode. Similar fact has also been observed previously for PtMo/C, Pt/Mo₂C/C and PtRu/C electrocatalyst, where the Pt cathode was contaminated by the Mo and Ru species after polarization measurements [22,62,142]. As in these cases the decay of the cell performance in the absence of CO is most probably due to the influence of W contaminants on the activity of oxygen reduction reaction, but the effect produced by the Mo is much more adverse than that produced here by W. However, Pt supported on tungsten carbide has shown a higher activity for electrochemical oxidation of hydrogen with and without CO than PtW/C catalyst. As catalyst support, WC/C is electrochemically more stable against oxidation than Vulcan XC-72 carbon. On the basis of potential cycling experiment applied to both Pt/WC/C and PtW/C electrocatalysts, it has been concluded that Pt/WC/C is significantly more stable than PtW/C.

Figure 47: TEM images of Pt/WC/C20 (a) and PtW/C (b) catalysts after testing.

Figure 48: Cyclic voltammograms of the Pt/C cathodes measured after 5000 potential cycles of the Pt/WC/C20, PtW/C and Pt/C anodes.

CHAPTER IV

CONCLUSIONS

5. Conclusions

Electrocatalysts with different catalyst supports (carbon, molybdenum carbide and tungsten carbide) were synthesized by the formic acid reduction method and tested for hydrogen oxidation in the presence of 100 ppm CO and stability as anode of proton exchange membrane fuel cell. The effect of heat treatment temperature on the PtMo/C catalyst activity and stability was studied. The heat-treated catalyst showed an enhanced CO tolerance and a better stability as compared to the as-prepared PtMo/C catalyst, particularly due to the stabilization of the catalyst particle sizes at high temperature. On the other hand the Pt supported on molybdenum carbide (Pt/Mo₂C/C), resulted in a higher activity for the hydrogen oxidation reaction in the presence of 100 ppm carbon monoxide, as compared to PtMo supported on carbon (PtMo/C) electrocatalyst. Potential cycling experiments showed that Pt/Mo₂C/C is significantly more stable than PtMo/C. Cyclic voltammetry and WDS analysis showed that all the Mo based electrocatalysts (PtMo/C, Pt/Mo₂C/C) suffered a partial dissolution of Mo during the cycling process, in which something of Mo crossed the electrolyte membrane and reached the cathode. Similarly, not only a higher CO tolerance but a greater stability was observed for the Pt supported on tungsten carbide (Pt/WC/C) as compared to PtW supported on carbon. The high stability and excellent hydrogen oxidation electrocatalytic activity of the carbide base electrocatalysts may be attributed to a high oxidation resistance of Mo₂C/C and WC/C than Vulcan-72 carbon. Polarization measurements and cyclic voltammetric results suggest that heat-treated PtMo/C, Pt/Mo₂C/C and Pt/WC/C electrocatalysts can be considered as an alternative electrocatalysts to improve the performance and durability of CO tolerant anodes in proton exchange membrane fuel cells.

6. Bibliographic References

1. LARMINIE, J.; DICKS, A. **Fuel cell systems explained**. 2nd ed. Chichester: John Wiley, 2001. 14 p.
2. BAGOTSKY, V. S. **Fuel cells problems and solutions**. 2nd ed. New York: John Wiley, 2012. 25 p.
3. CARRETTE, L.; FRIEDRICH, K. A.; STIMMING, U. Fuel cells-fundamentals and applications. **Fuel Cells**, v. 1, n. 1, p. 5-39, 2001.
4. RAYMENT, C.; SHERWIN, S. **Introduction to fuel cell technology**. Notre Dame: University of Notre Dame, 2003. 13 p.
5. AMOUROUX, J. **Green energy and technology**. London: Springer, 2006. 77 p.
6. SMITHA, B.; SRIDHAR, S.; KHAN, A. A. Solid polymer electrolyte membranes for fuel cell applications-a review. **Journal of Membrane Science**, v. 259, p. 10-26, 2005.
7. SAMMES, N.; BOVE, R.; STAHL, K. Phosphoric acid fuel cells: Fundamentals and applications. **Current Opinion in Solid State and Material Science**, v. 8, n. 5, p. 372-378, 2004.
8. PERRY, M. L.; FULLER, T. F. A historical perspective of fuel cell technology in the 20th century. **Journal of Electrochemical Society**, v. 149, n. 7, p. S59-S69, 2002.
9. DICKS, A. L. Molten carbonate fuel cells. **Current Opinion in Solid State and Material Science**, v. 8, n. 5, p. 379-383, 2004.
10. ORMEROD, R. M. Solid oxide fuel cells. **Chemical Society Review**, v. 32, n. 1, p. 17-28, 2003.
11. KUNZE, J.; STIMMING, U. Electrochemical versus heat-engine energy technology: a tribute to Wilhelm Ostwald's visionary statements. **Angewandte Chemie International Edition in English**, v. 48, n. 49, p. 9230-9237, 2009.
12. RALPH, T. R.; HOGARTH, M. P. Catalysis for low temperature fuel cells-cathode challenges. **Platinum Metal Review**, v. 46, n. 1, p. 3-14, 2002.
13. CHAE, K. J.; CHOI, M.; AJAYI, F. F.; PARK, W.; CHANG, I. S.; KIM, I. S. Mass Transport through a proton exchange membrane (Nafion) in microbial fuel cells. **Energy and Fuels**, v. 22, n. 11, p. 169-176, 2008.
14. HAMILTON, P. J.; POLLET, B. G. Polymer electrolyte membrane fuel cell (PEMFC) flow field plate: design, materials and characterisation. **Fuel Cells**, v. 10, n. 4, p. 489-509, 2010.

15. PEIGHAMBARDOUST, S. J.; ROWSHANZAMIR, S.; AMJADI, M. Review of the proton exchange membranes for fuel cell applications. **International Journal of Hydrogen Energy**, v. 35, n. 17, p. 9349-9384, 2010.
16. BASCHUK, J. J.; LI, X. Carbon monoxide poisoning of proton exchange membrane fuel cells. **International Journal of Energy Research**, v. 25, p. 695-713, 2001.
17. WEE, J. H.; LEE, K. Y. Overview of the development of CO-tolerant anode electrocatalysts for proton-exchange membrane fuel cells. **Journal of Power Sources**, v. 157, n. 1, p. 128-135, 2006.
18. THOMASON, A. H. **Increasing the CO tolerance of PEM fuel cell via current pulsing and self oxidation**. 2004. 75 f. Dissertation (Master of Science) - Texas A & M University, Texas, 2004.
19. ZHANG, J. **Investigation of CO Tolerance in Proton Exchange Membrane Fuel Cells**. 2004. 238 f. Thesis (Doctor of Philosophy in Chemical Engineering)-Worcester Polytechnic Institute, Worcester, 2004.
20. CHUNG, C.; CHEN, C.; WENG, D.; YAN, Y.; LIN, H. Investigation of cell operation conditions for CO tolerance improvement of PEMFC. **Journal of Chinese Society of Mechanical Engineers**, v. 28, n. 6, p. 563-569, 2007.
21. LENG, Y. J.; WANG, X.; HSING, I. M. Assessment of CO-tolerance for different Pt-alloy anode catalysts in a polymer electrolyte fuel cell using AC impedance spectroscopy. **Journal of Electroanalytical Chemistry**, v. 528, n. 1, p. 145-152, 2002.
22. NEPEL, T. C. M.; LOPES, P. P.; PAGANIN, V. A.; TICIANELLI, E. A. CO tolerance of proton exchange membrane fuel cells with Pt/C and PtMo/C anodes operating at high temperatures: A mass spectrometry investigation. **Electrochimica Acta**, v. 88, p. 217-224, 2013.
23. DAI, Y.; LIU, Y.; CHEN, S. Pt-W bimetallic alloys as CO-tolerant PEMFC anode catalysts. **Electrochimica Acta**, v. 89, p. 744-748, 2013.
24. MUKERJEE, S.; URIAN, R. C. Bifunctionality in Pt alloy nanocluster electrocatalysts for enhanced methanol oxidation and CO tolerance in PEM fuel cells: electrochemical and in-situ synchrotron spectroscopy. **Electrochimica Acta**, v. 47, n. 19, p. 3219-3231, 2002.
25. LIANG, Y.; ZHANG, H.; YI, B.; ZHANG, Z.; TAN, Z. Preparation and characterization of multi-walled carbon nanotubes supported PtRu catalysts for proton exchange membrane fuel cells. **Carbon**, v. 43, p. 3144-3152, 2005.
26. PAPAGEORGOPOULOS, D. C.; HEER, M. P.; KEIJZER, M.; PIETERSE, J. A. Z.; BRUIJN, F. A. Nonalloyed carbon-supported PtRu catalysts for PEMFC applications. **Journal of The Electrochemical Society**, v. 151, n. 5, p. A763-A768, 2004.

27. SCHMIDT, T. J.; NOESKE, M.; GASTEIGER, H. A.; BEHM, R. J.; BRITZ, P.; BONNEMANN, H. PtRu alloy colloids as precursors for fuel cell catalysts-A combine XPS, AFM, HRTEM and RDE study. **Journal of The Electrochemical Society**, v. 145, n. 3, p. 925-931, 1998.
28. PEREIRA, L. G. S.; SANTOS, F. R.; PEREIRA, M. E.; PAGANIN, V. A.; TICIANELLI, E. A. CO tolerance effects of tungsten-based PEMFC anodes. **Electrochimica Acta**, v. 51, n. 19, p. 4061-4066, 2006.
29. HAM, D. J.; KIM, Y. K.; HAN, S. H.; LEE, J. S. Pt/WC as an anode catalyst for PEMFC: Activity and CO tolerance. **Catalysis Today**, v. 132, n. 1-4, p. 117-122, 2008.
30. GUILLÉN-VILLAFUERTE, O.; GUIL-LÓPEZ, R.; NIETO, E.; GARCÍA, G.; RODRÍGUEZ, J. L.; PASTOR, E.; FIERRO, J. L. G. Electrocatalytic performance of different Mo-phases obtained during the preparation of innovative Pt-MoC catalysts for DMFC anode. **International Journal of Hydrogen Energy**, v. 37, n. 8, p. 7171-7179, 2012.
31. GRGUR, B. N.; ZHUANG, G. ; MARKOVIC, N. M.; ROSS, P. N. Electrooxidation of H₂/CO mixtures on a well-characterized Pt₇₅ Mo₂₅ alloy surface. **Journal of Physical Chemistry**, v. 5647, n. 97, p. 3910-3913, 1997.
32. CRABB, E. M.; RAVIKUMAR, M. K.; QIAN, Y.; RUSSELL, A. E.; MANIGUET, S.; YAO, J.; THOMPSETT, D.; HURFORD, M.; BALL, S. C. Controlled modification of carbon supported platinum electrocatalysts by Mo. **Electrochemistry Solid-State Letters**, v.5, n. 1, p. A5-A9, 2002.
33. HEO, P.; NAGAO, M.; SANO, M.; HIBINO, T. A high-performance Mo[sub 2]C-ZrO[sub 2] anode catalyst for intermediate-temperature fuel cells. **Journal of Electrochemical Society**, v. 154, n. 1, p. B53-B56, 2007.
34. KWIATKOWSKI, K. C.; MILNE, S. B.; MUKERJEE, S.; LUKEHART, C. M. Synthesis of Pt-Mo/Carbon nanocomposites from single-source molecular precursors: A (1:1) PtMo/C PEMFC anode catalyst exhibiting CO tolerance. **Journal of Cluster Science**, v. 16, n. 2, p. 251-272, 2005.
35. HU, J. E.; LIU, Z.; EICHHORN, B. W.; JACKSON, J. S. Nano-architected Pt-Mo anode electrocatalyst for high CO-tolerance in PEM fuel cells. **ECS Transaction**, v. 19, n. 31, p. 1-12, 2009.
36. WEIGERT, E. C.; ESPOSITO, D. V.; CHEN, J. G. Cyclic voltammetry and X-ray photoelectron spectroscopy studies of electrochemical stability of clean and Pt-modified tungsten and molybdenum carbide (WC and Mo₂C) electrocatalysts. **Journal of Power Sources**, v. 193, n. 2, p. 501-506, 2009.
37. MELLINGER, Z. J.; Weigert, E. C.; Stottlemeyer, A. L.; CHEN, J. G. Enhancing CO tolerance of electrocatalysts: electro-oxidation of CO on WC and Pt-modified WC. **Electrochemical and Solid-State Letters**, v. 11, n. 5, p. B63-B67, 2013.

38. MA, L.; ZHAO, X.; SI, F.; LIU, C.; LIAO, J.; LIANG, L.; XING, W. A comparative study of Pt/C and Pt-MoO_x/C catalysts with various compositions for methanol electro-oxidation. **Electrochimica Acta**, v. 55, n. 28, p. 9105-9112, 2010.
39. ORDÓÑEZ, L. C.; ROQUERO, P.; SEBASTIAN, P. J.; RAMÍREZ, J. Carbon-supported platinum-molybdenum electro-catalysts for methanol oxidation. **Catalysis Today**, v. 107-108, p. 46-52, 2005.
40. EHTESHAMI, S. M. M.; CHAN, S. H. A review of electrocatalysts with enhanced CO tolerance and stability for polymer electrolyte membrane fuel cells. **Electrochimica Acta**, v. 93, p. 334-345, 2013.
41. LOPES, P. P.; FREITAS, K. S.; TICIANELLI, E. A. CO Tolerance of PEMFC anodes: Mechanisms and electrode designs. **Electrocatalysis**, v. 1, n. 4, p. 200-212, 2010.
42. SANTIAGO, E. I.; BATISTA, M. S.; ASSAF, E. M.; TICIANELLI, E. A. Mechanism of CO tolerance on molybdenum-based electrocatalysts for PEMFC. **Journal of the Electrochemical Society**, v. 151, n. 7, p. A944-A949, 2004.
43. WATANABE, M.; UCHIDA, M.; MOT, S. Preparation of highly dispersed Pt + Ru alloy clusters and the activity for the electrooxidation of methanol. **Journal of Electroanalytical Chemistry**, v. 229, p. 395-406, 1987.
44. PEREIRA, L. G. S.; PAGANIN, V. A.; TICIANELLI, E. A. Investigation of the CO tolerance mechanism at several Pt-based bimetallic anode electrocatalysts in a PEM fuel cell. **Electrochimica Acta**, v. 54, n. 7, p. 1992-1998, 2009.
45. RUSSELL, A. E.; MANIGUET, S.; MATHEW, R. J.; YAO, J.; ROBERTS, M. A.; THOMPSETT, D. In situ X-ray absorption spectroscopy and X-ray diffraction of fuel cell electrocatalysts. **Journal of Power Sources**, v. 96, n. 1, p. 226-232, 2001.
46. MUKERJEE, S.; LEE, S. J.; TICIANELLI, E. A.; MCBREEN, J.; GRGUR, B. N.; MARKOVIC, N. M. Investigation of enhanced CO tolerance in proton exchange membrane fuel cells by carbon supported PtMo alloy catalyst. **Electrochemical and Solid-State Letters**, v. 2, n. 1, p. 12-15, 1999.
47. LAUSCHE, A. C.; MEDFORD, A. J.; KHAN, T. S.; XU, Y.; BLIGAARD, T.; ABILD-PEDERSEN, F.; NØRSKOV, J. K.; STUDDT, F. On the effect of coverage-dependent adsorbate-adsorbate interactions for CO methanation on transition metal surfaces. **Journal of Catalysis**, v. 307, p. 275-282, 2013.
48. ZHANG, S. YUAN, X. Z.; HIN, J. N. C.; WANG, H.; FRIEDRICH, K. A.; SCHULZE, M. A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells. **Journal of Power Sources**, v. 194, n. 2, p. 588-600, 2009.
49. WU, J.; YUAN, X. Z.; MARTIN, J. J.; WANG, H.; ZHANG, J.; SHEN, J.; WU, S.; MERIDA, W.; A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies. **Journal of Power Sources**, v. 184, p. 104-119, 2008.

50. HOLTON, O. T.; STEVENSON, J. W. The role of platinum in proton exchange membrane fuel cells. **Platinum Metal Review**, v. 57, n. 4, p. 259-271, 2013.
51. BORUP, R. L.; DAVEY, J. R.; GARZON, F. H.; WOOD, D. L.; INBODY, M. A. PEM fuel cell electrocatalyst durability measurements. **Journal of Power Sources**, v. 163, n. 1, p. 76-81, 2006.
52. KNIGHTS, S. D.; COLBOW, K. M.; ST-PIERRE, J.; WILKINSON, D. P. Aging mechanisms and lifetime of PEFC and DMFC. **Journal of Power Sources**, v. 127, n. 1-2, p. 127-134, 2004.
53. FERREIRA, P. J.; LA O', G. J.; SHAO-HORN, Y.; MORGAN, D.; MAKHARIA, R.; KOCHA, S.; GASTEIGER, H. A. Instability of Pt/C electrocatalysts in proton exchange membrane fuel cells. **Journal of the Electrochemical Society**, v. 152, p. A2256-A2271, 2005.
54. YOUSFI-STEINER, N.; MOÇOTÉGUY, P.; CANDUSSO, D.; HISSEL, D. A review on polymer electrolyte membrane fuel cell catalyst degradation and starvation issues: Causes, consequences and diagnostic for mitigation. **Journal of Power Sources**, v. 194, n. 1, p. 130-145, 2009.
55. YASUDA, K.; TANIGUCHI, A.; AKITA, T.; IOROI, T.; SIROMA, Z. Platinum dissolution and deposition in the polymer electrolyte membrane of a PEM fuel cell as studied by potential cycling. **Physical Chemistry Chemical Physics**, v. 8, n. 6, p. 746-52, 2006.
56. MEIER, J. C.; GALEANO, C.; KATSOUNAROS, I.; WITTE, J.; BONGARD, H. J.; TOPALOV, A.; BALDIZZONE, C.; MEZZAVILLA, S.; SCHÜTH, F.; MAYRHOFER, K. J. J. Design criteria for stable Pt/C fuel cell catalysts. **Beilstein Journal of Nanotechnology**, v. 5, p. 44-67, 2014.
57. SHAO-HORN, Y.; SHENG, W. C.; CHEN, S.; FERREIRA, P. J.; HOLBY, E. F.; MORGAN, D. Instability of supported platinum nanoparticles in low-temperature fuel cells. **Topics in Catalysis**, v. 46, n. 3-4, p. 285-305, 2007.
58. YU, K.; GROOM, D. J.; WANG, X.; YANG, Z.; GUMMALLA, M.; BALL, S. C.; MYERS, D.; FERREIRA, P. J. Degradation mechanisms of platinum nanoparticle catalysts in proton exchange membrane fuel cells: The role of particle size. **Microscopy and Microanalysis**, v. 20, n. S3, p. 482-483, 2014.
59. ZHANG, F. Y.; ADVANI, S. G.; PRASAD, A. K.; BOGGS, M. E.; SULLIVAN, S. P.; BEEBE, T. P. Quantitative characterization of catalyst layer degradation in PEM fuel cells by X-ray photoelectron spectroscopy. **Electrochimica Acta**, v. 54, n. 16, p. 4025-4030, 2009.
60. WESSELMARK, M. **Electrochemical reactions in polymer electrolyte fuel cells**. 2010. 63 f. Thesis (Doctor of Philosophy)-Applied Electrochemistry, School of Chemical Science and Engineering, Stockholm, 2010.

61. OTEGBADE, O. A. **Theoretical investigations of surface oxides on platinum and platinum alloy catalysts for fuel cell applications**. 2012. 212 f. Thesis (Doctor of Engineering)-Department of Earth Sciences, University College of London, London, 2012.
62. ANTOLINI, E. The problem of Ru dissolution from Pt-Ru catalysts during fuel cell operation: analysis and solutions. **Journal of Solid State Electrochemistry**, v. 15, n. 3, p. 455-472, 2010.
63. SEVJIDSUREN, G.; ZILS, S.; KASERER, S.; WOLZ, A.; ETTINGSHAUSEN, F.; DIXON, D.; SCHOEKEL, A.; ROTH, C.; ALTANTSOG, P.; SANGAA, D.; GANZORIG, C. Effect of different support morphologies and pt particle sizes in electrocatalysts for fuel cell applications. **Journal of Nanomaterials**, v. 2010, p. 1-9, 2010.
64. RODRIGUEZ, N. M.; CHAMBERS, A.; BAKER, R. T. K. Catalytic engineering of carbon nanostructures. **Langmuir**, v. 11, n. 10, p. 3862-3866, 1995.
65. TANIGUCHI, A.; AKITA, T.; YASUDA, K.; MIYAZAKI, Y. Analysis of electrocatalyst degradation in PEMFC caused by cell reversal during fuel starvation. **Journal of Power Sources**, v. 130, n. 1-2, p. 42-49, 2004.
66. RODRIGUEZ-REINOSO, F. The role of carbon materials in heterogeneous catalysis. **Carbon**, v. 36, n. 3, p. 159-175, 1998.
67. ANTOLINI, E. Carbon supports for low-temperature fuel cell catalysts. **Applied Catalysis B: Environmental**, v. 88, n. 1-2, p. 1-24, 2009.
68. AUER, E.; FREUND, A.; PIETSCH, J.; TACKE, T. Carbons as supports for industrial precious metal catalysts. **Applied Catalysis A: General**, v. 173, n. 2, p. 259-271, 1998.
69. SERP, P. Carbon nanotubes and nanofibers in catalysis. **Applied Catalysis A: General**, v. 253, n. 2, p. 337-358, 2003.
70. DOU, M.; HOU, M.; ZHANG, H.; LI, G.; LU, W. A highly stable anode carbon-free catalyst support based on tungsten trioxide nanoclusters for proton- exchange membrane fuel cells. **ChemSusChem**, v. 5, n. 5, p. 945-951, 2012.
71. PATT, J.; JU, D.; PHILLIPS, C.; Thompson, L. Molybdenum carbide catalysts for water - gas shift. **Catalysis Letters**, v. 65, p. 193-195, 2000.
72. CELZARD, A.; MARÊCHÉ, J. F.; FURDIN, G.; FIERRO, V.; SAYAG, C.; PIELASZEK, J. Preparation and catalytic activity of active carbon-supported Mo₂C nanoparticles. **Green Chemistry**, v. 7, n. 11, p. 784-792, 2005.
73. OYAMA, S. T. Preparation and catalytic properties of transition metal carbides and nitrides. **Catalysis Today**, v. 15, p. 179-200, 1992.
74. LEVY, R. The kinetics and mechanism of spillover. **Journal of Catalysis**, v. 32, n. 2, p. 304-314, 1974.

75. KIMMEL, Y. C.; XU, X.; YU, W.; YANG, X.; CHEN, J. G. Trends in electrochemical stability of transition metal carbides and their potential use as supports for low-cost electrocatalysts. **American Chemical Society Catalysis**, v. 4, n. 5, p. 1558-1562, 2014.
76. HU, F. P.; SHEN, P. K. Ethanol oxidation on hexagonal tungsten carbide single nanocrystal-supported Pd electrocatalyst. **Journal of Power Sources**, v. 173, n. 2, p. 877-881, 2007.
77. WEIGERT, E. C.; SMITH, N. A.; WILLIS, B. G.; AMORELLI, A.; CHEN, J. G. PVD synthesis and characterization of Pt-modified molybdenum carbides as potential electrocatalysts. **Electrochemical Solid-State Letters**, v. 8, n. 7, p. A337-A340, 2005.
78. LU, G.; COOPER, J. S.; MCGINN, P. J. SECM characterization of Pt-Ru-WC and Pt-Ru-Co ternary thin film combinatorial libraries as anode electrocatalysts for PEMFC. **Journal of Power Sources**, v. 161, n. 1, p. 106-114, 2006.
79. MENG, H.; SHEN, P. K. Tungsten carbide nanocrystal promoted Pt/C electrocatalysts for oxygen reduction. **Journal of Physical Chemistry**, v. 109, n. 48, p. 22705-22709, 2010.
80. CHHINA, H.; CAMPBELL, S.; KESLER, O. High surface area synthesis, electrochemical activity, and stability of tungsten carbide supported Pt during oxygen reduction in proton exchange membrane fuel cells. **Journal of Power Sources**, v. 179, n. 1, p. 50-59, 2008.
81. GANESAN, R.; HAM, D. J.; LEE, J. S. Platinized mesoporous tungsten carbide for electrochemical methanol oxidation. **Electrochemistry communication**, v. 9, n. 10, p. 2576-2579, 2007.
82. LEE, K.; ISHIHARA, A.; MITSUSHIMA, S.; KAMIYA, N. OTA, K. Stability and electrocatalytic activity for oxygen reduction in WC + Ta catalyst. **Electrochimica Acta**, v. 49, n. 21, p. 3479-3485, 2004.
83. MOON, J.; LEE, Y.; HAN, S.; PARK, K. Pd nanoparticles on mesoporous tungsten carbide as a non-Pt electrocatalyst for methanol electrooxidation reaction in alkaline solution. **International Journal of Hydrogen Energy**, v. 39, n. 15, p. 7798-7804, 2014.
84. MCINTYRE, D. R.; BURSTEIN, G. T.; VOSSEN, A. Effect of carbon monoxide on the electrooxidation of hydrogen by tungsten carbide. v. 107, p. 67-73, 2002.
85. YANG, X. G.; WANG, C. Y. Nanostructured tungsten carbide catalysts for polymer electrolyte fuel cells. **Applied Physics Letters**, v. 86, n. 22, p. 224104, 2005.
86. KELLY, T. G.; HUNT, S. T.; ESPOSITO, D. V.; CHEN, J. G. Monolayer palladium supported on molybdenum and tungsten carbide substrates as low-cost hydrogen evolution reaction (HER) electrocatalysts. **International Journal of Hydrogen Energy**, v. 38, n. 14, p. 5638-5644, 2013.

87. LIU, Y.; MUSTAIN, W. E. Evaluation of tungsten carbide as the electrocatalyst support for platinum hydrogen evolution/oxidation catalysts. **International Journal of Hydrogen Energy**, v. 37, n. 11, p. 8929-8938, 2012.
88. MUKERJEE, S.; URIAN, R. C.; LEE, S. J.; TICIANELLI, E. A.; MCBREEN, J. Electrocatalysis of CO tolerance by carbon-supported PtMo electrocatalysts in PEMFCs. **Journal of the Electrochemical Society**, v. 151, n. 7, p. A1094-A1103, 2004.
89. LEBEDEVA, N. P.; JANSSEN, G. J. M. On the preparation and stability of bimetallic PtMo/C anodes for proton-exchange membrane fuel cells. **Electrochimica Acta**, v. 51, n. 1, p. 29-40, 2005
90. HAN, K.; MOON, Y.; HAN, O.; HWANG, K.; KIM, I.; KIM, H. Heat treatment and potential cycling effects on surface morphology, particle size, and catalytic activity of Pt/C catalysts studied by ¹³C NMR, TEM, XRD and CV. **Electrochemistry Communication**, v. 9, n. 2, p. 317-324, 2007.
91. BEZERRA, C. W. B.; ZHANG, L.; LIU, H.; LEE, K.; MARQUES, A. L. B.; MARQUES, E. P.; WANG, H.; ZHANG, J. A review of heat-treatment effects on activity and stability of PEM fuel cell catalysts for oxygen reduction reaction. **Journal of Power Sources**, v. 173, n. 2, p. 891-908, 2007.
92. SANTOS, L. G. R. A.; FREITAS, K. S.; TICIANELLI, E. A. Heat treatment effect of Pt-V/C and Pt/C on the kinetics of the oxygen reduction reaction in acid media. **Electrochimica Acta**, v. 54, p. 5246-5251, 2009.
93. PRADO-BERGUETE, C.; LINARES-SOLANO, A.; RODRIGUEZ-REINOSO, F.; SALINA-MARTINEZ DE LECEA, C. The effect of oxygen surface groups of the support dispersion in Pt/Carbon catalysts on platinum. **Journal of Catalysis**, v. 115, p. 98-106, 1989.
94. COLOMA, F.; SEPÚLVEDA-ESCRIBANO, A.; FIERRO, J. L. G.; RODRIGUEZ-REINOSO, F. Preparation of platinum supported on pregraphitized carbon blacks. **Langmuir**, v. 12, p. 750-755, 1994.
95. STONEHART, P. Carbon substrates for phosphoric acid fuel cell cathodes. **Carbon**, v. 22, n. 4-5, p. 423-431, 1984.
96. ANTOLINI, E.; SALGADO, J. R. C.; GIZ, M. J.; GONZALEZ, E. R. Effects of geometric and electronic factors on ORR activity of carbon supported Pt-Co electrocatalysts in PEM fuel cells. **International Journal of Hydrogen Energy**, v. 30, p. 1213-1220, 2005.
97. ANTOLINI, E.; PASSOS, R. R.; TICIANELLI, E. A. Electrocatalysis of oxygen reduction on a carbon supported platinum -vanadium alloy in polymer electrolyte fuel cells. **Electrochimica Acta**, v. 48, p. 263-270, 2002.
98. MUKERJEE, S. Particle size and structural effects in platinum electrocatalysis. **Journal of Applied Electrochemistry**, v. 20, n. 4, p. 537-548, 1990.

99. MINAMI, R.; KITAMOTO, Y.; CHIKATA, T.; KATO, S. Direct synthesis of L10 type Fe-Pt nanoparticles using microwave-polyol method. **Electrochimica Acta**, v. 51, n. 5, p. 864-866, 2005.
100. NIE, M.; SHEN, P. K.; WU, M.; WEI, Z.; MENG, H. A study of oxygen reduction on improved Pt-WC/C electrocatalysts. **Journal of Power Sources**, v. 162, n. 1, p. 173-176, 2006.
101. SAVASTENKO, N. A.; BRÜSER, V.; BRÜSER, M.; ANKLAM, K.; KUTSCHERA, S.; STEFFEN, H.; SCHMUHL, A. Enhanced electrocatalytic activity of CoTMPP-based catalysts for PEMFCs by plasma treatment. **Journal of Power Sources**, v. 165, n. 1, p. 24-33, 2007.
102. SHIOYAMA, H.; HONJO, K.; KIUCHI, M.; YAMADA, Y.; UEDA, A.; KURIYAMA, N.; KOBAYASHI, T. C₂F₆ plasma treatment of a carbon support for a PEM fuel cell electrocatalyst. **Journal of Power Sources**, v. 161, n. 2, p. 836-838, 2006.
103. LIU, H.; SONG, C.; TANG, Y.; ZHANG, J.; ZHANG, J. High-surface-area CoTMPP/C synthesized by ultrasonic spray pyrolysis for PEM fuel cell electrocatalysts. **Electrochimica Acta**, v. 52, n. 13, p. 4532-4538, 2007.
104. CHENG, H.; YUAN, W.; SCOTT, K. Influence of thermal treatment on RuSe cathode materials for direct methanol fuel cells. **Fuel Cells**, v. 7, n. 1, p. 16-20, 2007.
105. HASSAN, A.; CARRERAS, A.; TRINCAVELLI, J.; TICIANELLI, E. A. Effect of heat treatment on the activity and stability of carbon supported PtMo alloy electrocatalysts for hydrogen oxidation in proton exchange membrane fuel cells. **Journal of Power Sources**, v. 247, p. 712-720, 2014.
106. CAMARA, G. A.; GIZ, M. J.; PAGANIN, V. A.; TICIANELLI, E. A. Correlation of electrochemical and physical properties of PtRu alloy electrocatalysts for PEM fuel cells. **Journal of Electroanalytical Chemistry**, v. 537, n. 1-2, p. 21-29, 2002.
107. SANTIAGO, E. I.; CAMARA, G. A.; TICIANELLI, E. A. CO tolerance on PtMo/C electrocatalysts prepared by the formic acid method. **Electrochimica Acta**, v. 48, n. 23, p. 3527-3534, 2003.
108. HYEON, T.; FANG, M.; SUSLICK, K. S. Nanostructured molybdenum carbide: Sonochemical synthesis and catalytic properties. **Journal of American Chemical Society**, v. 118, p. 5492-5493, 1996.
109. SUSLICK, K. S.; HYEON, T.; FANG, M.; AVE, S. M. Nanostructured materials generated by high-intensity ultrasound: Sonochemical synthesis and catalytic studies. **Chemistry Materials**, v. 8, n. 8, p. 2172-2179, 1996.
110. JOO, J. B.; KIM, J. S.; KIM, P.; YI, J. Simple preparation of tungsten carbide supported on carbon for use as a catalyst support in a methanol electro-oxidation. **Material Letters**, v. 62, n. 20, p. 3497-3499, 2008.

111. DYGAS, J.; KROK, F.; WIECZOREK, W.; MOSELEY, P.; CINDRELLA, L.; KANNAN, A. M. M.; LIN, J. F. F.; SAMINATHAN, K.; HO, Y.; LIN, C. W. W.; WERTZ, J. Gas diffusion layer for proton exchange membrane fuel cells-A review. **Journal of Power Sources**, v. 194, p. 146-160, 2009.
112. FADONI, M.; LUCARELLI, L. Temperature programmed desorption , reduction , oxidation and flow chemisorption for the characterisation of heterogeneous catalysts. Theoretical aspects , instrumentation and applications. **Studies in Surface Science and Catalysis**, v. 120, p. 1-45, 1999.
113. ALINK, R.; GERTEISEN, D. **Scanning Electron Microscopy**. New York: CRC, 2012. v. 1, p. 315-332.
114. ROLLER, J. **X-Ray Diffraction**. New York: CRC, 2012. v. 1, p. 289-313.
115. SALGADO, J. R. C.; GONZALEZ, E. R. Correlação entre a atividade catalítica e o tamanho de partículas de Pt/C preparados por diferentes métodos. **Eclética Química**, v. 28, n. 2, p. 77-85, 2003
116. WAGNER, C. D.; RIGGS, W. M.; DAVIS, L. E.; MOULDER, J. F. **Handbook of X-ray photoelectron spectroscopy**. Minnesota: Perkin-Elmer Corporation, 1979. 4 p.
117. LIN, R.; ZHENG, J.; MA, J. **Transmission Electron Microscopy**. New York: CRC, 2012. v. 1, p. 333-350.
118. NEWVILLE, M. **Fundamentals of XAFS**. Chicago: University of Chicago, 2004. 3 p.
119. BANG, J. H.; KIM, H. CO-tolerant PtMo/C fuel cell catalyst for H₂ oxidation. **Bulletin of the Korean Chemical Society**, v. 32, n. 10, p. 3660-3665, 2011.
120. CHRISTIEN, F.; FERCHAUD, E.; NOWAKOWSKI, P.; ALLART, M. **The use of electron probe microanalysis to determine the thickness of thin films in materials science**. Shangai: Intech, 2002. v. 1, p. 101-118.
121. ZHANG, D.; YUAN, X.; MA, Z. **Polarization Curve**. New York: CRC, 2012. v. 1, p. 15-35.
122. URIAN, R. C.; GULLÁ, A. F. MUKERJEE, S. Electrocatalysis of reformat tolerance in proton exchange membranes fuel cells: Part I. **Journal of Electroanalytical Chemistry**, v. 554-555, p. 307-324, 2003.
123. WU, J.; YUAN, X.; H. WANG. **Cyclic Voltammetry**. New York: CRC, 2012. v. 1, p. 71-85.
124. WANG, Z. B.; ZUO, P. J.; CHU, Y. Y.; SHAO, Y. Y.; YIN, G. P. Durability studies on performance degradation of Pt/C catalysts of proton exchange membrane fuel cell. **International Journal of Hydrogen Energy**, v. 34. p. 4387-4394, 2009.

125. ZHANG, S.; YUAN, X.; WANG, H.; MERIDA, W.; ZHU, H.; SHEN, J.; WU, S.; ZHANG, J. A review of accelerated stress tests of MEA durability in PEM fuel cells. **International Journal of Hydrogen Energy**, v. 34, n. 1, p. 388-404, 2009.
126. WANG, J.; LI, W.; YU, C.; CHEN, Y.; ZHANG, Y. Reducibility of Mo species in Pt/MoO₃ and PtMo/Al₂O₃ catalysis. **Reaction Kinetics and Catalysis Letters**, v. 62, n. 2, p. 217-224, 1997.
127. ARNOLDY, P.; JONGE, J. C. M.; MOULIJN, J. A. Temperature programmed reduction of MoO₃ and MoO₂. **Journal of Physical Chemistry**, v. 89, n. 1, p. 4517-4526, 1985.
128. WITKOWSKA, A.; PRINCIPI, E.; CICCIO, A. D.; DSOKE, S.; MARASSI, R.; OLIVI, L.; CENTAZZO, M.; ALBERTINI, V. R. Temperature and potential-dependent structural changes in a Pt cathode electrocatalyst viewed by in situ XAFS. **Journal of Non-Crystalline Solids**, v. 354, n. 35-39, p. 4227-4232, 2008.
129. PRINCIPI, E.; WITKOWSKA, A.; DSOKE, S.; MARASSI, R.; CICCIO, A. D. An XAS experimental approach to study low Pt content electrocatalysts operating in PEM fuel cells. **Physical Chemistry Chemical Physics**, v. 11, n. 43, p. 9987-95, 2009.
130. BALL, S.; HODGKINSON, A.; HOOGERS, G.; MANIGUET, S.; THOMPSETT, D.; WONG, B. The proton exchange membrane fuel cell performance of a carbon supported PtMo catalyst operating on reformat. **Electrochemical and Solid-State Letters**, v. 5, n. 2, p. A31-A34, 2002.
131. FERREIRA, P. J.; LA O', G. J.; SHAO-HORN, Y.; MORGAN, D.; MAKHARIA, R.; KOCHA, S.; GASTEIGER, H. A. Instability of Pt/C electrocatalysts in proton exchange membrane fuel cells-a mechanistic investigation. **Journal of Electrochemical Society**, v. 152, p. A2256-A2271, 2005
132. SCHAIDLE, J. A.; SCHWEITZER, N. M.; AJENIFUJAH, O. T.; THOMPSON, L. T. On the preparation of molybdenum carbide-supported metal catalysts. **Journal of Catalysis**, v. 289, p. 210-217, 2012.
133. PANG, M.; LI, C.; DING, L.; ZHANG, J.; SU, D.; LI, W.; LIANG, C. Microwave-assisted preparation of Mo₂C/CNTs nanocomposites as efficient electrocatalyst supports for oxygen reduction reaction. **Industrial and Engineering Chemistry Research**, v. 49, n. 9, p. 4169-4174, 2010.
134. SCHAIDLE, J. A.; LAUSCHE, A. C.; THOMPSON, L. T. Effects of sulfur on Mo₂C and Pt/Mo₂C catalysts: Water gas shift reaction. **Journal of Catalysis**, v. 272, n. 2, p. 235-245, 2010.
135. MANASILP, A.; GULARI, E. Selective CO oxidation over Pt/alumina catalysts for fuel cell applications. **Applied Catalysis B: Environmental**, v. 37, n. 1, p. 17-25, 2002.
136. STATE, S.; UNIT, S. C.; LUCIA, S.; BUILDING, B.; BRITAIN, G. Methanol electrooxidation on carbon-supported Pt-WO_{3-x} electrodes in sulphuric acid electrolyte. **Journal of Applied Electrochemistry**, v. 25, p. 528-532, 1995.

137. Yang, X. G.; Wang, C. Y. Nanostructured tungsten carbide catalysts for polymer electrolyte fuel cells Nanostructured tungsten carbide catalysts for polymer electrolyte fuel cells. *Applied Physics Letters*. v. 86, p. 224104, 2005.
138. ZELLNER, M. B.; CHEN, J. G. Surface science and electrochemical studies of WC and W₂C PVD films as potential electrocatalysts. **Catalysis Today**, v. 99, n. 3-4, p. 299-307, 2005.
139. BARNETT, C. J.; BURSTEIN, G. T.; KUCERNAK, A. R. J.; WILLIAMS, K. R. Electrocatalytic activity of some carburised nickel, tungsten and molybdenum compounds. **Electrochimica Acta**, v. 42, n. 15, p. 2381-2388, 1997.
140. ZAYAT, M.; REISFELD, R.; MINTI, H.; OREL, B.; SVEGL, F. Gasochromic effect in platinum-doped tungsten trioxide films prepared by the sol-gel method. **Journal of Sol-Gel Science and Technology**, v. 11, p. 161-168, 1998.
141. CHHINA, H.; CAMPBELL, S.; KESLER, O. Thermal and electrochemical stability of tungsten carbide catalyst supports. **Journal of Power Sources**, v. 164, n. 2, p. 431-440, 2007.
142. HASSAN, A.; PAGANIN, V. A.; CARRERAS, A.; TICIANELLI, E. A. Molybdenum carbide-based electrocatalysts for CO tolerance in proton exchange membrane fuel cell anodes. **Electrochimica Acta**, v. 142, p. 307-316, 2014.