

STUDY OF THE MICROSTRUCTURE AND PROPERTIES OF A
PEMFC CATALYST LAYER

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ABSTRACT

In this thesis, the microstructure and performance of Proton Exchange Membrane Fuel Cells (PEMFCs) with platinum (Pt)-metal-group-free and Pt-based electrodes are evaluated to analyze the effect of the catalyst composition and structure on the electrode properties. In PEMFC systems, the thickness, structure and morphology of the catalyst layer (CL) are integral to cell performance and are particularly significant for cathodes using a non-precious metal catalyst due to higher catalyst loadings and thicker catalyst layers that compensate for the relatively low catalytic activity. An iron (III) porphyrin framework material was synthesized, pyrolyzed and its activity for the oxygen reduction reaction evaluated as a function of the catalyst loading (electrode thickness) and oxygen partial pressure. Various polarization losses were decoupled to reveal limiting processes. The kinetic overpotential was the major contributor. Mass transport contributions to voltage loss increased with higher cathode catalyst loading. Observed performance is discussed in the context of CL structure and morphology, analyzed using microscopy and X-Ray Diffraction. For Pt-based electrodes, the effects of the carbon support and the CL composition were experimentally studied. Machine-prepared cathode CLs with different Pt to carbon (Pt:C) ratios on highly graphitized carbon were prepared using a fixed 3M ionomer to carbon ratio. These were characterized and their PEMFC performance was evaluated. The Pt:C ratio had a significant influence on the CL structure and

transport properties. The lowest Pt:C ratio (30:70) exhibited a higher volume of secondary pores and higher proton conductivity over the whole relative humidity range, with higher performance in PEMFC. This correlated with a more homogeneous ionomer distribution throughout the CL, caused by a preferential ionomer/carbon affinity. A study of interactions between 3M ionomer adsorption on a series of carbon supports with various Pt:C ratios provided further evidence for higher affinity of ionomer to the carbon surface. The adsorption isotherm for ionomer on carbon was quantified with two methods. Preferential adsorption on amorphous/graphitic carbon structure boundaries was confirmed. Ionomer adsorption occurs mainly on the secondary pores surface, consistent with previous BET results. Pt nanoparticles exhibited a negative effect on the adsorption process, possibly by blocking ionomer adsorption preferential sites.

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Chapter 1

INTRODUCTION

Fuel cells (FCs) are energy conversion devices allowing the direct conversion of chemical energy to electrical energy. The FC operating principle was conceived by Sir William Grove in 1839,¹ stating: electrolysis could be performed in reverse with the aid of a catalyst, producing electricity.²

In the early 1960s, General Electric developed what would later be known as the polymer electrolyte membrane or proton exchange membrane fuel cells (PEMFCs), characterized by a thin solid membrane ($\leq 50 \mu\text{m}$) which functions as an electrolyte and by low operating temperatures ($60\text{-}80^\circ\text{C}$). Sulfonated polystyrene membranes were originally used as electrolytes for this application; however, Nafion[®] membranes replaced sulfonated polystyrene in 1966, given their chemical and thermal stability and high proton conductivity.³

As shown in Figure 1, PEMFCs are composed of a polymer membrane, placed between two porous electrodes. This arrangement is known as the membrane electrode assembly (MEA). The energy conversion in a PEMFC occurs through a series of electrochemical reactions, which take place at the interface between an electrode and the membrane in the catalyst layer (CL). The CL is defined as the region where electrochemical reactions take place. Both hydrogen oxidation at the anode and oxygen reduction at the cathode reactions require a catalytic material to break the molecular bond of the diatomic gaseous reactant molecules, given the low-temperature conditions in a PEMFC.² The oxygen reduction reaction (ORR), in particular, represents a major voltage loss in PEMFCs, due to its slower reaction

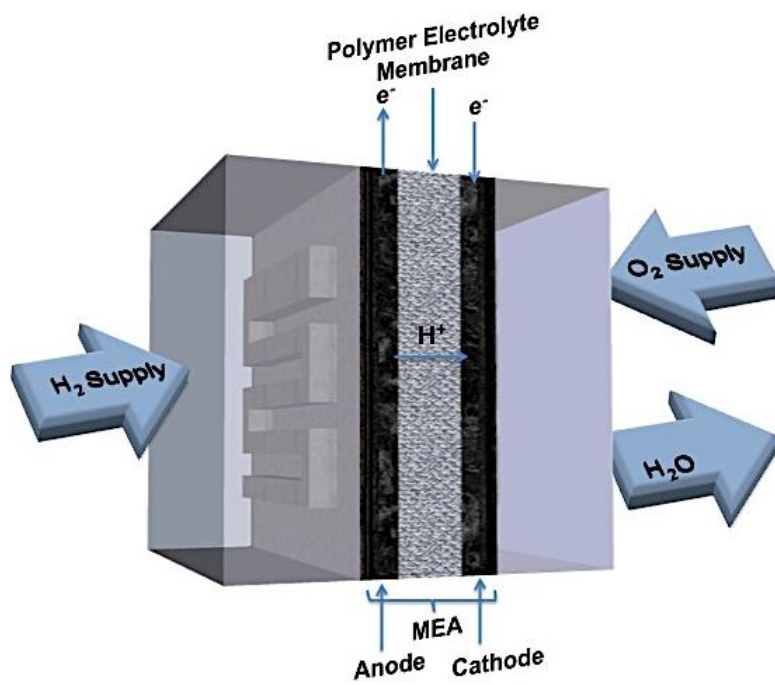


Figure 1. Diagram of PEMFC principle

rate and higher overpotential when compared to the hydrogen oxidation reaction (HOR).

The CL functions also include mass transport of the reactants, proton transport and electron conduction. Each function is necessary for a reaction to occur on the catalyst surface. Therefore, the catalyst utilization would be determined by the satisfaction of three criteria: gas access, proton access and electronic path continuity. These, in turn, are determined by the structure and composition of the CL.⁴

Despite the significant advancement in CL design and catalyst utilization, large-scale commercialization of PEMFC technology demands further development to meet durability and overall-cost requirements. To overcome these challenges, a profound understanding of the structure and transport properties of the various components is required.

Factors such as the structure of the support are critical for the resulting electrode structure. Soboleva et al. studied the microstructure of CLs containing two commonly used carbon supports (Ketjenblack and Vulcan XC-72), finding that the character of carbon particle aggregation of the support was preserved in the CL structure.⁵

Regarding the binder, many studies have been focused on determining the optimal composition, mainly working with perfluorosulfonic acid (PFSA) ionomers such as

Nafion. A 30 wt.% (dry weight of ionomer/total CL dry weight) content has been determined to provide a continuous proton conduction network without blocking the gas transport pathway.⁶ However, this parameter does not provide insight on the transport phenomena occurring in the CL, but instead has shown dependence on factors like carbon support structure and ionomer equivalent weight.⁶ The influence of the carbon support has been attributed to the structure and size distribution of the support that would define the resultant distribution of the ionomer within the pores.

The binder type also plays an important role in the CL properties, influencing permeability, catalytic activity, ionic conductivity, durability, etc. Different alternatives to the standard PFSA ionomer (Nafion) have been evaluated, including shorter-side chain and low equivalent weight PFSA, like the 3M ionomer (Figure 2), and sulfonated hydrocarbon polymers, such as s-PEEK (sulfonated poly ether ketone) and s-PSU(sulfonated polysulfone).⁷

In this work, the microstructure and performance of PEMFCs with platinum-group-metal (PGM)-free and Pt-based electrodes have been evaluated to analyze the effect of the catalyst composition and structure on the electrode properties. The complete methodology followed is presented in Chapter 2.

Chapter 3 presents a detailed discussion of the effect of macroscopic parameters such as electrode thickness and composition when the cathode catalyst is based

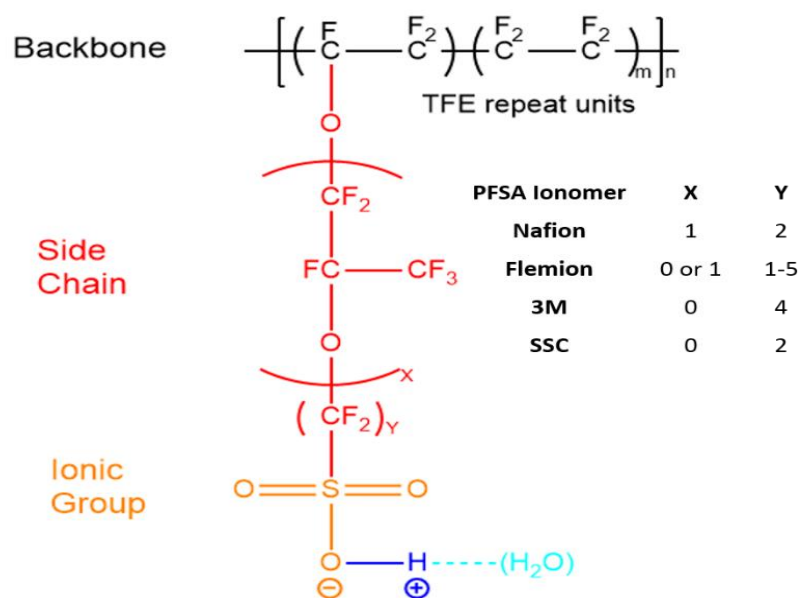


Figure 2. General chemical formula for PFSA ionomers chemical formula.

on a non-precious metal. For this purpose, an iron (III) porphyrin framework material was synthesized and pyrolyzed and, subsequently, evaluated as a catalyst towards the ORR. The single cell performance of this PGM-free electrode was evaluated as a function of the electrode catalyst loading (electrode thickness) and oxygen partial pressure. As expected, the ORR kinetic overpotential was the major contributor to the overall voltage loss. However, the mass transport contribution to the voltage loss became more prominent with small increases in the cathode catalyst loading. The observed performance is discussed in the context of structure and morphology of the CL, analyzed through scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-Ray Diffraction (XRD).

Chapter 4 focuses on the characterization of the properties of machine-prepared cathode CLs formed with different Pt to C (Pt:C) ratios, a highly graphitized carbon (EA carbon) and 3M ionomer (825EW) with a fixed ionomer to carbon (I:C) ratio. SEM, TEM and Brunauer-Emmett-Teller (BET) nitrogen adsorption were conducted to investigate the CCL microstructure including material dispersion and porosity. This analysis was performed on both the CL in an as-prepared condition and after being subjected to a standard PEMFC protocol. The Pt:C ratio had a significant influence on the CCL structure and transport properties. The lowest Pt:C ratio (30:70) exhibited a higher volume of secondary pores and a higher proton conductivity over the whole relative humidity (RH) range. Such behavior was

associated with a more homogeneous ionomer distribution throughout the CCL and resulted in an enhanced PEMFC performance. A high volume of macropores and high ionomer proton conductivity are correlated with the highest cell performance achieved with the lowest Pt:C ratio tested.

Chapter 5 is focused on the study of the interactions between 3M 825 equivalent weight (EW) ionomer and different carbon supports: Vulcan XC-72, Black Pearls 2000, Ketjenblack (KJB), and acetylene black. A series of in-house prepared Pt:C (0:100, 30:70, and 50:50 Pt:C ratios) samples using Vulcan XC-72 was also evaluated to further understand this interaction. The adsorption isotherm of water-dissolved 3M 825 EW ionomer on both the carbon supports and a series of VulcanXC72-supported platinum catalysts were studied, using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) to quantitatively analyze the adsorption process. Progress toward developing methods for studying polymer adsorption onto supports using ^{19}F Nuclear Magnetic Resonance Spectroscopy (NMR) is also reported. A detailed structure characterization of the pristine supports and catalyst materials was achieved through BET nitrogen adsorption-desorption, TEM, XRD and Raman Spectroscopy. The adsorbed ionomer structure was also explored through SSNMR. A significant effect of the carbon support structure and the pore size network on the ionomer adsorption was found.

Chapter 2

OVERVIEW OF METHODOLOGY

Different experimental techniques used in the development of this study are introduced in this chapter, along with the experimental protocols.

2.1 Catalyst Synthesis

2.1.1 PGM-free Catalyst Synthesis and activation

The covalent heme framework (CHF-1) catalyst was prepared according to the procedure described previously.⁸ Briefly, iron(III) tetra (4-bromophenyl)porphyrin chloride was added to a solution of 2,2'-bipyridyl, bis(1,5-cyclooctadiene)-nickel(0) and 1,5-cyclooctadiene in anhydrous DMF/1,4-dioxane. This mixture was stirred at room temperature under argon atmosphere overnight, and subsequently cooled in an ice bath. Finally, a 50% acetic acid solution was added, and the resulting mixture was stirred for another night and then washed and dried in vacuum to give CHF-1 in 78% yield.

The prepared catalyst was thermally activated under inert atmosphere (N₂ gas) at a wide range of temperatures (600°C-1000°C) for 1 hour. The optimal temperature at this stage was determined based on the electrocatalytic activity of the pyrolyzed materials. Following, the optimal material was subjected to an acid treatment in 0.5 M H₂SO₄ at 80 °C for 8 hours, with the purpose of removing metal particles generated during pyrolysis.⁹ Then the sample was subjected to a second heat treatment at the optimal temperature for 1 hour in an inert atmosphere to promote the formation of additional catalytic centers.¹⁰

2.1.2 Pt-based Catalysts Synthesis

The 3M adsorption behavior on in-house prepared catalysts was studied and is reported in Chapter 5. Carbon-supported platinum catalysts were prepared by the vapor deposition technique as described previously.^{11,12} Briefly, Vulcan carbon XC-72 was combined with solid Pt(acac)₂ (ACROS Organics) in the appropriate ratio in a fixed bed reactor and heated to 210°C in a N₂-water vapor atmosphere.

2.2 Physicochemical Characterization

Information on the distribution of individual components and global structural properties is acquired through a series of experimental techniques, which are described in detail in this section.

2.2.1 Scanning Electron Microscopy (SEM)

For SEM imaging, a Hitachi S-4800 field emission scanning electron microscope was employed. This equipment features a resolution of 1.0 nm and a variable acceleration voltage of 0.5-30 kV. The Hitachi S-4800 is equipped with both a lower and an upper secondary electron (SE) detector system.

Both SE and backscattered electron (BSE) signals can be individually detected or combined to obtain information on the sample. SE provides high-resolution information on the surface of the sample while BSE provides a higher sensitivity to compositional information as well as information on specimen depth. Macroscopic

properties such as CCL thickness, and morphology can be evaluated with this technique.

2.2.2 Transmission Electron Microscopy (TEM)

TEM is a powerful characterization technique that allows structure characterization and component identification at a nm scale in a variety of sample types.

2.2.2.1 PGM-free catalysts characterization

The synthesized CHF-1 catalyst powders were diluted in methanol and a drop of this solution was placed on a 300-mesh copper grid. Information regarding composition of the materials was obtained via EDX characterization. Furthermore, identification and visualization of the carbon structure and iron particles in the sample was achieved through this technique.

2.2.2.2 Pt-based-free-standing electrodes characterization and Pt size distribution

For catalyst layer studies, TEM has been conducted on powders scraped from the composite electrodes, with the main objective of characterizing the electrocatalyst.^{13–15} However this methodology is not able to provide information on the overall CL structure, given the loss of spatial integrity.¹⁶ Standard diamond-knife sectioning of epoxy-embedded MEAs allows preservation of the 3-layer structure and cross-sectional visualization of the CL.¹⁷

Samples for this study have been prepared through both scraping and epoxy-embedding techniques:

- The catalytic material was scraped from the freestanding electrodes to visualize the electrocatalyst material. The scraped material was then diluted in methanol and a drop of this solution was placed on a 300-mesh copper grid.
- A small piece of the MEA was removed and embedded in an epoxy resin. Samples were then microtomed at room temperature using a Leica UCT. Araldite was used as the embedding material. The Araldite in the impregnated MEA was polymerized at 60°C for 24 hours in a vacuum oven.

All samples were examined in a Hitachi HF-3300 300 kV TEM/STEM (scanning transmission electron microscope) with a cold-field emission gun and 0.13 nm resolution. This technique allows the microstructure characterization of the CCLs in terms of Pt size distribution, ionomer distribution, pore size Distribution and carbon support structure.

Given the high Pt atomic number and the contrast differences with the other CL components, it is possible to evaluate Pt sizes and distributions from the TEM images. To this effect, many TEM images from different areas of both fresh and post-operation CLs were acquired. ImageJ® was used to manually count the

individual particles, guaranteeing that a large number of particles (>1000) was counted in each sample.

This parameter was analyzed for both fresh (pristine) and post-FC operation electrodes, to study the changes that the electrode undergoes during standard operation. The Statgraphics® software was used to process the results obtained. To compare and study the statistical distributions, two shape parameters were calculated: standardized skewness and standardized kurtosis.

The standardized skewness (z_1) is a measure of the asymmetry of the data distribution, calculated according to Equation [1]:^{18,19}

$$z_1 = \frac{\frac{n \sum_{i=1}^n (x_i - \bar{x})^3}{(n-1)(n-2)s^3}}{\sqrt{6/n}} \quad [1]$$

Where n is the number of observations, x_i is the i^{th} observation, $\bar{x}$ is the average or arithmetic mean, and s is the standard deviation. Positive skewness indicates a longer upper tail than lower, while negative skewness indicates a longer lower tail. At the 5% significance level, significant skewness could be asserted if the value of z_1 fell outside the interval (-2, +2).

The standardized kurtosis (z_2) is a measure of the relative peakedness or flatness compared to a normal (bell-shaped) curve:^{18,19}

$$z_2 = \frac{\frac{n(n+1) \sum_{i=1}^n (x_i - \bar{x})^4}{(n-1)(n-2)(n-3)s^4} - \frac{3(n-1)^2}{(n-2)(n-3)}}{\sqrt{24/n}} \quad [2]$$

A value close to 0 correspond to a nearly bell-shaped normal distribution. A positive z_2 value corresponds to a distribution that is more peaked in the center and has longer tails than the normal; whereas a negative z_2 value indicate a flatter distribution than the normal with shorter rails. At the 5% significance level, significant kurtosis could be asserted if z_2 fell outside the interval (-2, +2).

2.2.3 X-Ray Diffraction (XRD)

The XRD technique provides information on the structure of crystalline materials, in terms of interatomic distances and bond angles. This analysis is based on the constructive interference of monochromatic X-rays passing through the crystalline sample when Bragg's Law (Equation [3]) is satisfied.

$$n\lambda = 2d\sin\theta \quad [3]$$

Where λ corresponds to the wavelength of the electromagnetic radiation, d is the lattice spacing in the crystalline sample and θ is the diffraction angle.

In this study, the well-known Scherrer equation (Equation [4]) has been used to calculate catalyst particle size:²⁰

$$L = \frac{K\lambda}{\beta \cos\theta} \quad [4]$$

In which L is the mean size of the crystalline domains, K is a numerical factor which depends on the actual shape of the crystallite, and β is the half-value breadth of the diffracted beam.

XRD patterns were measured with a Bruker D2 Phaser diffractometer with Cu K α radiation.

2.2.4 Gas Sorption Technique

The surface area and the pore size distribution (PSD) of the catalysts were measured with a Quantachrome Instruments Autosorb iQ with nitrogen as the adsorbate. BET and Barrett-Joyner-Halenda (BJH) Pore Size ND Volume Analysis was employed to analyze this data.

The BET theory, which is based upon the phenomenon of physical adsorption of gases on the external and the internal surfaces of a porous material, was applied for specific surface area determination.²¹ This theory leads to the calculation of W_m , the weight of the adsorbate constituting a monolayer of surface coverage (Equation [5]), which is proportional to the total external and internal surface of the material.²²

$$\frac{W}{W_m} = \frac{C(P/P_0)}{(1 - P/P_0)(1 + (C - 1)P/P_0)} \quad [5]$$

Where W is the weight of gas adsorbed at a relative pressure P/P_0 and the term C is a constant related to the extent to which the heat of adsorption in the first layer exceeds the latent heat of condensation of bulk adsorbate.^{21,23}

As mentioned before, the BHJ method was used to calculate pore size distributions. This method is based on a model of the adsorbent as a collection of cylindrical pores, taking into account both the effect of capillary condensation in the pores and of the thinning of the adsorbed layer.^{24,25}

2.2.5 Inductively Coupled Plasma/Optical Emission Spectrometry

An Agilent 5110 SVDV ICP-OES instrument was employed to perform ICP-OES. This technique was used to quantify the iron content in the PGM-free catalysts at different stages of the sample activation.

2.3 Electrochemical Characterization

2.3.1 PGM-free catalysts characterization

2.3.1.1 Rotating Ring Disk Electrode (RRDE) experiments

Inks were prepared by mixing 5 mg of the catalysts with 5 wt. % Nafion solution (Sigma-Aldrich) in a 30/70 ionomer to catalyst ratio, with methanol as the solvent. Inks were stirred for at least one day and sonicated for 10 minutes before preparing

the electrodes. 15 μL of the ink was deposited on a glassy carbon (GC) electrode disk to achieve loadings of $600 \mu\text{g}\cdot\text{cm}^{-2}$. A typical three-electrode cell system with a gold wire counter electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode saturated with 0.5 M H_2SO_4 was used. The potential of the reference electrode vs. the reversible hydrogen electrode (RHE) was measured experimentally by saturating the electrolyte with hydrogen for at least 30 minutes and measuring the open circuit potential using a Pt working electrode. The potential was determined to be 0.696 V vs. RHE. All potentials are reported vs. RHE.

The working electrode consisted of a GC disk with a Pt ring (AFE7R9GCPT from Pine Instruments) with a collection efficiency of 37%. The electrode potential was controlled using a multi-channel VSP3 potentiostat from BioLogic Science Instruments. The rotation speed of the working electrode was controlled with an AFMSRCE Pine Modulated Speed Rotator (MSR) and held constant at 1600 rpm. The experiments were conducted in a 0.1 M H_2SO_4 solution at room temperature. Voltammograms were collected at $10 \text{ mV}\cdot\text{s}^{-1}$ scan rate, static and rotating, with the electrolyte saturated with nitrogen, for background correction, and oxygen. Before each experiment, the GC disk was mechanically polished with 5 μm and 0.05 μm size alumina powder.

RDE experiments were performed in solutions of electrolyte saturated with oxygen at different oxygen partial pressures. For this purpose, oxygen and argon were

mixed using two high precision Cole-Parmer multi-gas MC series mass flow controllers. The partial pressure of oxygen was varied from 5 to 100%.

2.3.1.2 Membrane Electrode Assembly Preparation

To prepare electrodes for the FC experiments, cathode catalyst inks were prepared. A preliminary study was carried out to determine the best ionomer (Nafion) ratio in terms of fuel cell performance. Three different catalyst inks were prepared with a fixed catalyst powder amount (15 mg), 1 ml of deionized water, 2 ml of isopropanol and a variable weight of Nafion solution. The Nafion to catalyst ratios were set to 30:70, 50:50 and 70:30, and the catalyst loading on the cathode electrode was $2\text{mg}_{\text{cat}}\cdot\text{cm}^{-2}$ for this comparison. The inks were sprayed onto a 5 cm^2 gas diffusion layer (GDL) using an airbrush, until the desired catalyst loading was reached.

After determining the ‘optimal’ ionomer content, different catalyst loadings were evaluated ($1\text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$, and $3\text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$). The cathode CL thickness was measured for each loading, using an Absolute Mitutoyo® Digimatic Indicator (Model ID-S112PE).

GDLs made of carbon paper with a carbon coating (SIGRACET® Gas Diffusion Media, Type GDL 25 BC) were used for both electrodes. The anode electrodes, on the other hand, were prepared by hand painting. The anode ink was prepared from BASF 30% Pt on Vulcan XC-72. Anode loadings were $0.3\text{ mg}_{\text{Pt}}\cdot\text{cm}^{-2}$ with a

2:1 ionomer to Pt ratio. The cathode and anode electrodes were hot-pressed against either side of a 212 Nafion membrane at 140°C for 10 minutes using a load of 1000 kg.

2.3.1.3 *Fuel Cell Testing*

Single cell experiments on the prepared MEAs were performed using a Fuel Cell Technologies test stand and single cell hardware. A BioLogic VSP3 potentiostat with a 10 A booster was used to collect polarization curves and electrochemical impedance spectroscopy (EIS) data. The cell has a serpentine flow channel and an active area of 5 cm². The temperature for all experiments was 80 °C, backpressure at both electrodes was 29.4 bar psia, and all gases were at 100% RH. The flow rate of ultra-high purity (UHP) H₂ at the anode was held constant at 0.1 L min⁻¹ and UHP O₂ flow was kept at 0.2 L min⁻¹.

The testing protocol was the following: The cell was held at open circuit voltage (OCV) for 10 minutes; then the voltage was held at 0.6 V for 15 mins, followed by 0.4 V for 10 mins for conditioning. A polarization curve was obtained by changing the potential from OCV to 0.2 V, decreasing the potential in steps of 2 mV from OCV to 0.65 and 20 mV from 0.65 V to 0.2 V, each potential was held constant for 30 seconds before recording the current. Measurements were performed with different oxygen partial pressures in the cathode feed, ranging from 20 to 100%,

obtained by mixing oxygen and argon gases, as described above. All overpotentials are reported using the reversible OCV as reference.

To evaluate the behavior of our catalyst in an actual fuel cell, we need to disentangle kinetic and mass transport effects. We do this using a series of approaches. First, we compare the polarization curves obtained for a series of different loadings of 'catalyst'. Since we do not know the total number of catalyst sites in the catalyst used, we simply refer to the loading of carbon powder containing the active sites formed during pyrolysis. We have also increased the number of data points obtained in the kinetic region of the polarization curve. This region is generally underdetermined in most polarization studies of FCs regardless of catalyst type, resulting in a lack of data points for fitting of kinetic parameters. We also use oxygen partial pressure as a variable to generate additional information about both kinetics and mass transport.

2.3.1.4 Polarization Study

Single cell experiments on the prepared MEAs were performed using a Fuel Cell Technologies test stand and single cell hardware. A BioLogic VSP3 potentiostat with a 10 A booster was used to collect polarization curves and EIS. The cell has a serpentine flow channel and an active area of 5 cm².

The temperature for all experiments was 80 °C, backpressure at both electrodes was 29.4 bar psig, and all gases were at 100% RH. The flow rate of UHP H₂ at the

anode was held constant at 0.1 L min⁻¹ and UHP O₂ flow at the cathode was kept at 0.2 L min⁻¹. The anode acts as both the counter and reference electrode, while the cathode is the working electrode in this setup.

The testing protocol was the following: The cell was held at OCV for 10 minutes, then the voltage was held at 0.6 V for 15 mins, followed by 0.4 V for 10 mins for conditioning. A polarization curve was obtained by changing the potential from OCV to 0.2 V, decreasing the potential in steps of 2 mV from OCV to 0.65 and 20 mV from 0.65 V to 0.2 V, each potential was held constant for 30 seconds before recording the current.

Polarization curves were recorded under different RH and O₂ partial pressure conditions for MEAs with either Pt-based or NPMCs cathodes.

2.3.2 Pt-based catalysts characterization

2.3.2.1 Polarization Study

A polarization study was carried out to investigate the electrochemical performance of the free-standing 3M CLs. MEAs were prepared by hot-pressing the freestanding electrodes at one side of a Nafion 212 membrane at 140°C for 10 min with a 1000 kg load. Subsequently, an in-house prepared electrode was hot-pressed to the other side of the membrane, along with a GDL against the cathode side.

The in-house anodes were prepared by mixing 10 mg of 30:70 w/w Pt:C Tanaka® catalyst powder, with 1 ml of isopropanol and 122 mg of 5 wt. % Nafion solution. The ink was sprayed onto a 5 cm² GDL using an airbrush. Ink was sprayed onto the substrate until a 0.2mg_{Pt}·cm⁻² catalyst loading was reached. GDLs made of carbon paper with a carbon coating (SIGRACET Gas Diffusion Media, Type GDL 25 BC) were used for both electrodes.

With the prepared MEAs, single cell experiments were performed using a Fuel Cell Technologies test stand and single cell hardware. A BioLogic VSP3 potentiostat with a 10A booster was used to collect polarization curves and potentiometric-electrochemical impedance spectroscopy (PEIS). The cell has a serpentine flow channel and an active area of 5 cm².

To study the polarization behavior, measurements in both H₂/O₂ and H₂/air were performed at 80°C cell temperature and 13psi/13psi backpressure. Gas flows in the anode and cathode sides were 100sccm/200sccm respectively, for both the H₂/O₂ and H₂/air systems. Each cell system was conditioned overnight at 60% RH following the same protocol: the cell was held at OCV for 10 min, then at 0.6 V for 15 min, followed by 0.4 V for 10 min. Next, polarization curves were obtained by decreasing the potential in steps of 0.002 V from OCV to 0.65V and in steps of 0.02 V from 0.65V to 0.2 V. Each potential was held constant for 30 s before recording the current. Measurements were performed at different RH values, ranging from 35 to 100%. After each RH shift, the cell rested for 45 min at OCV to

reach equilibrium before data acquisition. All overpotentials are reported using the reversible OCV as reference.

2.3.2.2 Cyclic Voltammetry (CV)

The CV technique consists of a linear potential sweep between two set voltage limits (-0.2 to 1.2V), while current is recorded. A low potential scan rate ($v = 0.01 \text{ V s}^{-1}$) is held in order to minimize impedance losses.²⁶ This technique is used to estimate the electrochemically active surface area ($ECSA [=] \text{cm}^2_{Pt} g_{Pt}^{-1}$) and the double layer capacitance (CDL).²⁷ During this process, the setup is similar to that used in the polarization curves acquisition; the only variation being that the cathode compartment is fed with a 0.2 L min^{-1} UHP N_2 flow.

With the charge density ($q_{Pt} [=] \text{C cm}^{-2}_{electrode}$) obtained from the hydrogen adsorption process in the CV experiment, it is possible to calculate the ECSA of the Pt catalyst:

$$ECSA = \frac{q_{Pt}}{\Gamma \cdot L} \quad [6]$$

Using the characteristic value of charge density associated with a monolayer of hydrogen adsorbed on polycrystalline platinum ($\Gamma = 210 \mu\text{C} \cdot \text{cm}^{-2}$) and the Pt loading in the cathode or working electrode ($L [=] \text{g}_{Pt} \text{ cm}^{-2}$).²⁸

On the other hand, the C_{DL} calculation (Equation [7]) requires the measurement of i_{DL} , the current in the double-layer region ($0.4\text{V} < E < 0.6\text{V}$) which takes into

account the capacitive current due to charging/discharging of the electrical double layer and the transport limited H₂ crossover current.²⁷

$$i_{DL} = C \frac{dE}{dt} = C_{DL} \cdot v \quad [7]$$

2.3.3 Electrochemical Impedance Spectroscopy

In EIS, a small amplitude alternating current (AC) perturbation with a variable frequency is added to a constant direct current (DC).²⁹ By this method, the impedance change can be registered and the different components related with each process (charge transfer, mass transfer, electrolyte resistance, adsorption of electroactive species, etc.) can be calculated.

2.3.3.1 High-frequency resistance measurements

EIS measurements were carried out through a BioLogic VSP3 potentiostat with a 10 A booster on the Fuel Cell setup described. All AC impedance spectra reported here were measured between the fuel cell cathode and the fuel cell anode. The EIS measurements were carried out at each point of the polarization curve. The frequency scan was performed from 10 kHz down to 1 Hz.

2.3.3.2 Proton Conductivity Measurements

This technique has been particularly useful for in-situ CL proton resistance measurements.³⁰ For these measurements, we used the same system described

in the polarization curves section. After acquiring the polarization curves, the cell was changed to the H₂/Nitrogen(N₂) system and was held at OCV and 60% RH for a 12 h period, to eliminate O₂ gas from the pipelines and cathode compartment. PEIS measurements were then performed at the same RH range used for polarization experiments. The frequency ranged from 0.5 Hz to 20 kHz with a 0.03V perturbation. H₂ and N₂ gases were both fed at 100 mL·min⁻¹, and the cell was held at 80°C and 0.2V. After each RH shift, the cell rested for 45 min at OCV to reach equilibrium before data acquisition. EIS was performed at 0.2 V, imposing a 10-mV AC signal and a frequency range of 200 kHz to 1 Hz using a BioLogic VSP3 potentiostat.

The CL proton conductivity can then be calculated from the Nyquist plot which typically exhibits two characteristics behaviors: a 45° angle region at high to intermediate frequencies due to proton resistance in the CL and a 55-90° angle in the lower frequency region representing the CL capacitance and resistance.^{27,29–31} The CL proton resistance, R_P can be obtained from the extrapolation of both slopes to the real impedance axis.^{27,29,30}

$$R_P = 3(Z'_{LF} - Z'_{HF}) \quad [8]$$

Where Z'_{LF} and Z'_{HF} corresponds to the low and high frequency intercepts at the real part of the impedance, respectively. These measurements were averaged over 3 repetitions.

2.4 Water Uptake Measurements

To perform λ measurements in the free-standing electrodes, each electrode was transferred onto a Kapton[®] film. The purpose of this transfer was to provide mechanical stability to the thin electrodes. All samples were hot-pressed at 120°C for 15 min. Then, the CL/Kapton system was dried by suspending it over a volume of phosphorous pentoxide (P₂O₅) for a period of 7 days. The dried samples were suspended over lithium chloride (LiCl) solutions with different concentrations over 7 days. Excess water was removed with the aid of Kimwipes. After reaching equilibrium, the final weight of the sample (W_{wet}) was registered.

Through this methodology, samples with different hydration levels were obtained, and λ was calculated using the equation:

$$\lambda = \frac{\frac{(W_{wet} - W_{dry})}{W_{dry}} \times EW \times 100}{M_{H_2O} \times Ionomer \text{ wt}\%}} \quad [9]$$

Where W_{dry} corresponds to the sample weight after dehydration over P₂O₅, EW to the equivalent weight of the ionomer in the CL, M_{H_2O} to the molecular weight of water and *Ionomer wt%* to the weight percentage of ionomer in the dry sample.

2.5 3M Ionomer Adsorption Study

2.5.1 3M Ionomer Solutions Preparation

3M ionomer solutions of different concentrations (between 0.25 and 8 g_{3MIon}·l⁻¹) were prepared from an aqueous 16% wt. 3M 825 EW ionomer solution. Dilution of the solution to the desired concentrations was followed by 20 mins of ultrasonication and 30 min of 24 h of mechanical shaking to guarantee homogenization of the ionomer solutions.

2.5.2 Adsorption Experiment

The adsorption of 3M ionomer was studied in different substrates. First, the adsorption on carbon supports was analyzed: Vulcan carbon XC-72 (V72), KJB, acetylene black (AB), and Black-Pearls (BP). Then, the adsorption on V72-supported Platinum materials was studied: 30 and 50% Pt/V72.

The 3M ionomer solutions prepared as described above were mixed with 6 mg of each substrate. The mixtures were then subjected to 15 mins of ultrasonication and 24 h of mechanical shaking. Following, the mixtures were centrifuged at 4°C for 1 h at 1200 rpm. The resulting supernatant solution was filtered through a Nylon Filter Media with a 0.2 µm pore size and subsequently analyzed through NMR and ICP-OES experiments.

2.5.3 Nuclear Magnetic Resonance (NMR)

To perform the NMR experiments, 600 μl of each filtered solution was placed on an 5 mm NMR tube, and 20 μl of trifluoroacetic acid (CF_3COOH) was added as internal reference.^{32,33}

All NMR experiments were performed on a Varian Unity 400 MHz instrument spectrometer operating at ^{19}F frequency of 370.275 MHz. The temperature was stabilized at 26 °C. NMR spectra were acquired in series with auto sampler with $d1=8.0$ s, $AQ=8.72$ s, and a total of 2800 scans. Signal base line correction, chemical shift corrections and peak integration was achieved using Mnova[®] software.

2.5.4 Inductively-Coupled Plasma Optical Emission Spectroscopy

Standard ICP-OES solutions were prepared to obtain the sulfur (S) concentration calibration plot. The standard solutions were prepared by dilution of a Sigma-Aldrich[®] Sulfur Standard for ICP (10,000 ppm S in water) solution with a HNO_3 solution to stabilize elements in solution. The final sulfur concentrations ranged from 0 to 0.020 $\text{gS}\cdot\text{l}^{-1}$. Sulfur detection was performed at 181.973 nm wavelength.

An Agilent 5110 SVDV ICP-OES instrument was used to analyze the equilibrium solution concentrations. For this purpose, 1.2 ml of the filtered solution was mixed with 1.8 ml of a 5% HNO_3 solution to minimize matrix variation effects. The 3M

ionomer equilibrium concentration (C_{3Meq}) was calculated from the detected sulfur concentration (C_S) as shown in Equation [10].

$$C_{3Meq} \left[\frac{g_{3M}}{l} \right] = C_S \left[\frac{g_S}{l} \right] \cdot EW_{3M} \left[\frac{g_{3M}}{mol_{SO_3^-}} \right] \cdot MW_S^{-1} \left[\frac{mol_{SO_3^-}}{g_S} \right] \quad [10]$$

2.5.5 Adsorption Parameters Estimation

To compare the relative interaction strength and surface coverage, the adsorption equilibrium constant (K_{eq}) and the maximum surface coverage (Γ_{max}) were calculated by fitting to the Langmuir equation:

$$\Gamma_{eq} = \frac{\Gamma_{max} \cdot K_{eq} \cdot C_{eq}}{1 + K_{eq} \cdot C_{eq}} \quad [11]$$

Where C_{eq} corresponds to the 3M equilibrium concentration and Γ_{eq} to the equilibrium surface coverage.

The adsorption parameters were estimated using the *nlinfit* function in Matlab®, given that the model is not linear in the K_{eq} parameter (the second derivative of Γ_{eq} with respect to K_{eq} does not equal zero). An initial estimate ($[\Gamma_{max}; K_{eq}] = [0.01; 0.01]$) was used resulting in a good convergence and low correlation.

The standard error σ_i of each parameter was estimated from the variance-covariance matrix:

$$covB = (X^T X)^{-1}(MSE) = \begin{pmatrix} \sigma_{\Gamma_{max}} & \sigma_{\Gamma_{max}K_{eq}} \\ \sigma_{\Gamma_{max}K_{eq}} & \sigma_{K_{eq}} \end{pmatrix} \quad [12]$$

Where σ_i corresponds to the square root of the corresponding diagonal of the symmetric parameter variance-covariance matrix and X is the Jacobian.

2.5.6 Solid State Nuclear Magnetic Resonance (SSNMR)

Solid-state ^{19}F NMR spectra of the ionomer adsorbed on the carbon samples were acquired using a Bruker Avance III spectrometer with a 400MHz (^1H frequency) magnet using a 4 mm Magic Angle Spinning broad band probe (zirconia rotors). The samples for this experiment were obtained through the adsorption experiment described previously (Section 2.5). However, the ionomer solution concentration was significantly increased (16 wt. %) to enhance the signal-to-noise ratio. After the centrifugation step, the substrate/ionomer solid was filtered and dried under vacuum at a 90°C temperature overnight. Finally, the dry sample was mixed with a silicon nitride (Si_3N_4) powder in a 1:1 mass ratio. The purpose of the Si_3N_4 addition is to separate the carbon particles and decrease the electronic conductivity of the sample.

The mixture was spun at the magic angle at a rate of 15 kHz at 25°C. The ^{19}F chemical shift was referenced to ammonium trifluoroacetate at -140 ppm. A single

pulse sequence was employed to record these data with a recycle delay (d_1) of 10s. 64 scans were accumulated for reasonable signal-to-noise ratio.

Chapter 3

INVESTIGATION OF A MICROPOROUS IRON (III) PORPHYRIN FRAMEWORK DERIVED CATHODE CATALYST IN PEM FUEL CELLS

A version of this chapter was originally published by N. M. Cantillo, G. A. Goenaga, W. Gao, K. Williams, C. A. Neal, S. Ma, K. L. More, and T. A. Zawodzinski:

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Data acquisition (including physicochemical characterization of the material, and testing) for this article was performed entirely by Nelly Cantillo. The conception and design of the study was done by Nelly Cantillo in conjunction with Dr. Gabriel Goenaga, and Dr. Thomas Zawodzinski. Dr. Ma, Dr. Gao and Mrs. Williams at the University of South Florida prepared and provided the material to be tested. Mr. Christopher Neal cooperated with fuel cell setup and experiments.

Data analysis was performed by MSc. Nelly Cantillo and Dr. Thomas Zawodzinski. Dr. Karren More collaborated with the microscopy data interpretation. Nelly Cantillo prepared the draft of the manuscript and along with Dr. Thomas Zawodzinski revised the manuscript thoroughly before submission. Approval of the final version of the manuscript to be published involved all authors

Abstract

In Proton Exchange Membrane Fuel Cells, the thickness, structure and morphology of the electrode CL are integral to cell performance. The effect of these

parameters become particularly significant when the cathode catalyst is based on a non-precious metal due to the higher catalyst loadings required to compensate for the lower catalytic activity when compared to Pt based catalysts. In this study, an iron (III) porphyrin framework material was synthesized and pyrolyzed and its catalytic activity towards the oxygen reduction reaction (ORR) was evaluated using rotating disk electrode experiments and single cell testing. Single cell performance was evaluated as a function of the electrode catalyst loading (electrode thickness) and oxygen partial pressure. As expected, the ORR kinetic overpotential was the major contributor to the overall voltage loss. However, the mass transport contribution to the voltage loss became more prominent with small increases in the cathode catalyst loading. The observed performance is discussed in the context of structure and morphology of the CL, analyzed through scanning electron microscopy, transmission electron microscopy, and X-Ray Diffraction.

3.1 Introduction

The sluggish ORR accounts for most of the voltage loss in PEMFCS, even when the best Pt-based catalysts are employed.³⁴ This factor and the low availability and high cost of Pt, have motivated the search for PGM-free catalysts to decrease cost and facilitate PEMFC commercialization. Although significant progress has been made in increasing PGM-free catalyst activity, translating this into a high-performance PEMFC still remains a challenge. For 2020, the US Department of

Energy (DOE) have established a $>0.044 \text{ A}\cdot\text{cm}^{-2}$ catalyst activity target at 0.9 V_{IR-free} for a transportation PEMFC stack.³⁵

The complete ORR involves the transfer of four electrons and four protons leading to production of water. This transfer, however, does not occur in a single reaction step and various reaction pathways have been considered.^{36–41} In acid solutions, the ORR generally involves the generation of a desorbed hydrogen peroxide (H₂O₂) intermediate. This indirect pathway can occur on the same type of active site or on sites of different natures (bifunctional mechanism).^{42,43} In PGM-free catalyst research, the nature of the active sites where this reaction occurs is still a matter of significant debate.

3..1.1 PGM-free catalyst activity and stability

Among the evaluated PGM-free catalyst alternatives, those derived from heat-treated metal/nitrogen/carbon (Me-N-C) compounds have produced the best ORR activity results.^{44–51} Jasinski's 1964 paper jump-started the study of ORR catalysis on N₄-metal chelates thanks to his promising results on the activity of cobalt phthalocyanine (CoPc) in alkaline medium.⁵² Following work, by Jahnke et al., demonstrated that several MePc exhibited ORR activity in acidic media with a strong dependence on the central metal atom ($\text{Cu} \approx \text{Ni} < \text{Co} < \text{Fe}$).⁵³ Later, the improvement of ORR catalytic activity and, more importantly, catalyst stability via a thermal pretreatment in an inert gas constituted a significant breakthrough in the PGM-free catalyst development.^{53,54} This discovery raised many questions, whose

answers are still under debate, regarding the role of the heat treatment in the active site formation and the structure of this site.

The heat-treatment temperature has a significant influence on the resulting catalyst activity. In general, the best ORR activity results were obtained with 500-600 °C temperatures, while optimal stability was achieved with pyrolysis temperatures up to 900 °C.^{9,54} Different hypotheses were proposed to explain this trend. Early studies by Yeager et al. suggested that decomposition of Me-N₄ chelates would take place at temperatures as low as 400-500 °C, dismissing the idea that Me-N₄ are essential for ORR catalysis. This claim was supported by Mössbauer measurements obtained with iron(III) tetramethoxyphenylporphyrin (FeTMPP) and Co-TMPP, which did not exhibit a signal indicating the presence of nitrogen-coordinated metals after treatment at 800 °C in argon.^{55,56}

Van Veen et al. on the other hand, claimed that although high temperature pyrolysis can lead to decomposition of the Me-N₄ sites, pyrolysis at low temperature (500-600 °C) does not involve destruction of the macrocycles.^{57,58} They based their conclusions on X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), Mössbauer, and extended X-ray absorption fine structure spectroscopy (EXAFS) characterization in a series of Me-chelate precursors.^{58,59} Furthermore, the stability improvement is explained by bonding of the reactive parts of the ligand to the carbon which leads to lower susceptibility to oxidative attack.

Although early studies mainly focused on materials obtained from transition-metal-based macrocycles,^{52,60} preparation of catalysts from pyrolyzed separate metal, nitrogen, and carbon precursors has been widely explored since 1989.⁶¹ This approach offers a great variety of possibilities for precursors and synthesis conditions. The precedent for this method was set by Yeager et al., who reported the use of poly(acrylonitrile) (PAN) and a metal precursor (cobalt or iron) loaded onto a carbon support and pyrolyzed at 800°C in argon.⁶¹ The materials obtained exhibited ORR activity comparable to that of heat-treated cobalt porphyrins.

Yeager's work motivated the subsequent study of many other N-containing compounds, including polymers as dual carbon and nitrogen precursors, which can facilitate the formation of N-containing sites on the graphitic carbon surface during the catalyst synthesis.¹⁰ Studies involving PAN plus metal have been reported, emphasizing the importance of the simultaneous presence of the metal salt and the nitrogen precursor during the heat treatment process.^{62–64} Some of this work explored PAN-based nanostructured materials, such as aerogel composites,⁶³ N-doped ordered porous carbons,⁶⁴ and carbon-nitride(CN_x)/PAN nanofibers⁶⁵ as catalyst precursors. Substantial ORR activities were reported. Lalande et al. explored the role and importance of the presence of different atoms (N, metal or both) in the generation of the catalytic site by employing polyvinylferrocene as a nitrogen-free precursor.⁶⁶ The material obtained through a single-step pyrolysis did not exhibit any catalytic activity for the ORR. However,

it was possible to obtain an active catalyst through a second pyrolysis step in the presence of a nitrogen source such as acetonitrile vapor, which further emphasized that both N and Fe precursors play a role in the formation of the ORR active site.

Heterocyclic polymers, particularly pyrrole derivatives, have also been widely studied as N-containing precursors since 1990.^{64,67–74} This provides the possibility to mimic the atomic configuration of Me-containing porphyrins. It is assumed that the metal atom bonds to pyrrole units, allowing the formation of Me-N sites upon pyrolysis.⁷⁰ Major progress in achieving fuel-cell-relevant performance through this approach was reported with the publication from Wood et al.⁷⁵ In this case, nitroaniline was mixed with an anhydrous metal salt (generally an iron chloride) and polymerized in the presence of carbon, activated by firing in the presence of ammonia, and ball-milled and subjected to an optional second firing, which proved to be beneficial for the catalytic activity. Finally, the milled catalyst was acid washed to remove the leachable portion of transition metals. The material showed high ORR onset voltages, above 0.9 V, and a volumetric current density of 19 A cm⁻³ at 0.8V. This study constituted one of the first efforts in PEMFC testing of non-precious catalysts, highlighting the effect of mechanical treatment of the catalyst (i.e. ball-milling) and catalyst loading.

Significant improvement has been achieved with PGM-free catalysts prepared using heterocyclic polymers such as polyaniline (PANI) as precursors^{10,44,76–79}.

Zelenay's group reported a comparison of PANI and polypyrrole (PPy) as nitrogen precursors for iron-based-catalyst synthesis, obtaining better performance with respect to stability and selectivity with the former.⁷⁶ Promising durability results were obtained with PANI-FeCo-C catalysts (700-hour-fuel cell performance test at a constant cell voltage of 0.4 V). These materials were synthesized by mixing a short-chain aniline oligomer with high-surface area carbon material, and transition metal precursors, followed by the addition of an oxidant to polymerize the aniline. After polymerization, water was removed, and the sample was subjected to a 900°C heat treatment under a N₂ atmosphere, leached in H₂SO₄ for 8 hours and subsequently subjected to a second heat treatment. High power density (0.38 W cm⁻² at 0.6 V) was reached in fuel cell operation (H₂-O₂) with these materials.⁴⁴ PANI-based nanostructured materials have also been studied with promising results.^{65,78} XPS, XRD and HRTEM analysis in PANI-based catalysts evinces the presence of transition metals on the catalyst surface and their interaction with both nitrogen and carbon precursors. This behavior is in contrast to reports where no metal was detected in the treated catalysts,^{80,81} and was ascribed to the aromatic character of PANI. The PANI is alleged to have a stronger bond to the carbon support and this, in turn, facilitates the electron transfer from the metal site to the oxygen.

Advances have also been made through the enhancement of the mass-transport properties of the catalyst material.^{48,64,79,82–85} In particular, metal-organic

frameworks (MOFs) have been employed due to the accessibility of metal cation in their structure, high volumetric density of metal-ion sites and high micropore surface area.^{86,87} Liu and co-workers were the first to implement this approach, selecting a cobalt-based zeolitic imidazolate framework (ZIF, a subclass of MOFs with imidazolate as ligand) as a precursor for the synthesis of ORR catalysts through pyrolysis.^{82,83} Maximum performance, with an onset potential of 0.83 V, was achieved after pyrolysis at a temperature of 750°C, comparable to the best cobalt-based PGM-free catalysts.⁸⁸ In 2011, Dodelet's group selected a Zn-based ZIF, covered with a small amount of iron-phenanthroline complex as catalyst precursor.⁴⁹ A power density of 0.91 W cm⁻² at 0.6 V (H₂/O₂, 1 bar gauge pressure, 4mg cm⁻²), comparable to that of a state-of-the-art Pt-based cathode having a loading of 0.3 mg_{Pt} cm⁻², was reported with this material. However, the stability tests showed a significant decay in current density over 100 h of operation. Recent studies with this material have involved the use of an iron porphyrin (as iron and nitrogen precursor), in order to study the effect of the pyrolysis temperature on the resulting stability.⁸⁷ The significant improvement obtained with MOFs underlined the importance of the catalyst structure and, particularly, of the pore network for the resulting performance of the catalyst.

As an additional approach, amorphous porous organic polymers (POPs), have been extensively studied over the last decade.^{8,89–92} Catalysts derived from these precursors exhibit exceptional characteristics of surface area, uniform pore sizes,

and stability. Recently, Ma et al. reported the construction of a porphyrin-based conjugated porous organic polymer, named CHF-1, utilizing a custom-designed porphyrin complex, iron (III) meso-5,10,15,20-tetrakis (4-bromophenyl)porphyrin chloride (Fe(tbpp)Cl), as a building block.⁸ This material was designed as a biomimetic oxidation catalyst, but its potential as an ORR catalyst is investigated in this work.

3.1.2 Degradation of PGM-free Catalysts

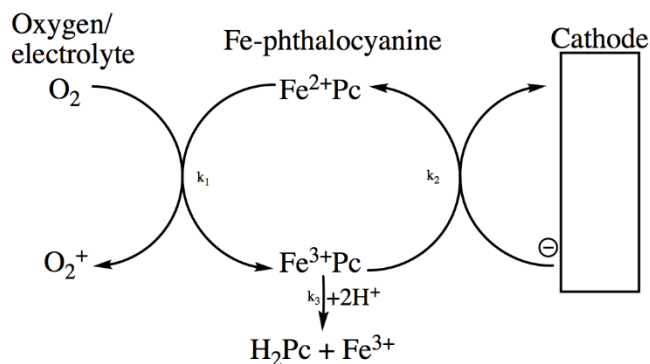
Lack of stability, understood as the performance loss during galvanostatic experiments, is one of the main challenges for PGM-free catalysts development. Different degradation mechanisms have been proposed in the literature but understanding of this phenomenon is far from complete.^{76,81,101–103,93–100} In this section, we will discuss some of the major mechanisms proposed in the literature.

3.1.2.1 Leaching of the PGM-free catalyst

Phenomena such as carbon corrosion can lead to leaching of the metal particles present in PGM-free catalysts.^{61,93,97–100,104} This mechanism increases in significance in prolonged fuel cell operation. Operando spectroscopic analysis with a variety of Fe-N-C structures has shown that its contribution is negligible in short durability tests (5-50 h).⁹⁸

Earlier studies pointed to the FeN₄ macrocycles as the main demetallation sources.^{105,106} The behavior of polymeric iron phthalocyanine (Pc) catalysts during

the ORR in H₂SO₄ has been studied by Meier et al. and Baranton et al. through ⁵⁹Fe radiotracer and Mössbauer experiments and *in situ* infrared reflectance (IR) spectroscopy experiments, respectively. Both approaches revealed significant catalyst demetallation in oxygen-containing H₂SO₄ solution. An electron transfer from the central iron atom to the oxygen molecule was proposed (equation [13]), which would increase the oxidation state of the iron atom from 2 to 3 and lead to a decrease of the atomic radius, and therefore make It less stable in the macrocycle.⁹³ The IR experiments revealed the formation of free base phthalocyanine (H₂Pc), which has low activity towards ORR, during chronoamperometry experiments.^{105,107}



This analysis, however, was derived from experiments with well-defined non-pyrolyzed macrocycles supported on carbon. After pyrolysis, as illustrated in Figure 3 for the case of PANI-Fe-C catalysts, active Fe-N-C materials become

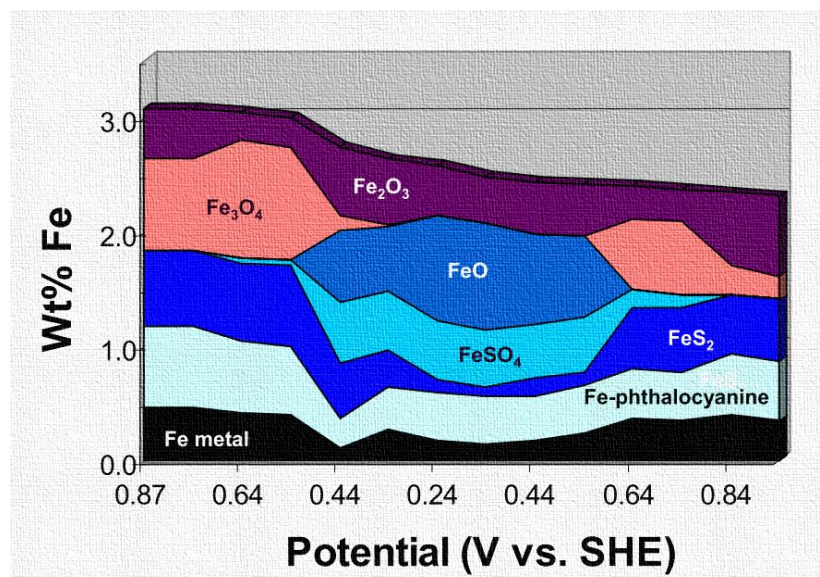


Figure 3. Coordination environment and oxidation state of Fe species in PANI-Fe-C as a function of potential in 0.5 M H₂SO₄, as determined from linear combination fitting of Fe K-edge X-ray absorption spectra to Fe standards (reproduced from Wu et al.).⁷⁶

complex and polymorphic in nature, involving a great variety of Fe species (metallic Fe, Fe oxides, carbines, Fe-N-C moieties), which might limit the applicability of this analysis.^{76,98}

The thermodynamic instability of metallic Fe and Co under typical PEMFC conditions (Figure 4) has motivated their dismissal as active catalyst components. Consequently, acid-washing has been adopted as a common practice in PGM-free catalysts synthesis to eliminate the leachable metallic particles.^{40,44,108,109} Bulk metal content reduction though this technique has been observed through ICP technique. The leaching occurs without affecting the catalyst activity.^{81,93,98} A recent study by Choi et al., however, suggests that acid washing is not able to fully dissolve inactive Fe particles exposed to the electrolyte.⁹⁸ Using a scanning flow cell connected to an inductively coupled plasma mass spectrometer (SFC/ICP-MS), continuous Fe leaching was detected below 0.7 V_{RHE} with a flow of 0.1 M HClO₄. In contrast, *ex situ* electrochemical CV and chemical control of open circuit potential were suggested as more effective ways to remove inactive Fe species from the catalyst surface.

3.1.2.2 *Hydrogen peroxide attack*

The oxidative attack of PGM-free catalysts by H₂O₂, which is one possible product of the ORR, has been explored as a possible degradation mechanism for the last five decades.^{37,101,110,111} Schulenburg et al. proposed that H₂O₂ can directly oxidize the N-atoms bounded to the metal center, leading to dissolution of the oxidized N

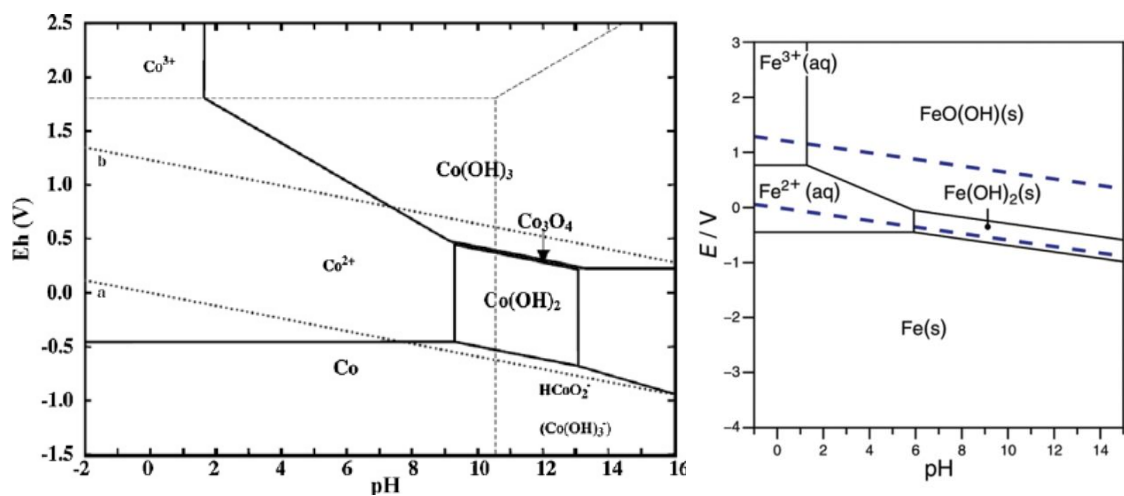
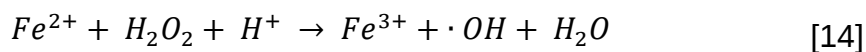
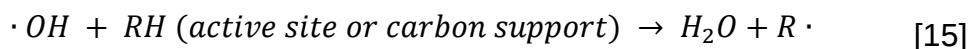


Figure 4. Pourbaix diagrams of Co (left) and Fe (right) in H₂O systems.

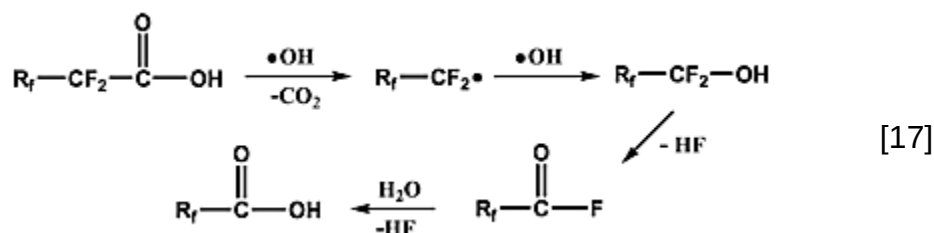
species into the surrounding ionomer/electrolyte phase and to the associated reduction in catalytic activity.¹¹¹ Based on Mössbauer spectroscopy and XPS experiments, the authors speculated that the active site in a heat-treated FeTMPP-chloride (Cl) catalyst corresponds to a 6-fold coordinated Fe³⁺ compound. It is important to note, however, that these conclusions were drawn from an *ex situ* characterization and the presence of the proposed nitrogen oxidation products was not identified. Further exploration would be required to validate this hypothesis. Decomposition of H₂O₂, on the other hand, can also lead to the formation of highly reactive free radicals, such as the hydroxyl ·OH and the hydroperoxyl HOO· free radicals.^{9,112} The combination of H₂O₂ and Fe²⁺ is known as a Fenton's reagent.^{9,113} Therefore, any trace of Fe²⁺ can lead to H₂O₂ decomposition through the Fenton's reaction (equation [14]).



Although HOO· radicals are also formed during H₂O₂ decomposition, they have been found to be significantly less reactive than the hydroxyl free radical.¹¹⁴ As suggested by Dodelet's group in 2006, Fenton's reaction (equation [14]) will be followed by:⁹



Beyond its potential to degrade catalyst structure, the hydroxyl radical can attack the carboxylic end-groups in PFSA ionomers (equation [17]), leading to main chain degradation, as was proposed by Curtin et al. and discussed elsewhere.^{115,116}



3.1.2.3 Protonation and anion adsorption

Recently, two mechanisms have been proposed as explanations for the sharp performance loss observed over the first hours (~2h) of PEMFC operation (region I in Figure 5).^{102,117} Popov's group associated this early-stage degradation with protonation of pyridinic and quaternary nitrogen, which are presented as the active sites for ORR.^{64,117,118} The argument regarding the metal-free nature of the active sites is based on earlier studies in their group where significant catalytic activity was obtained with metal-free nitrogen-modified carbon-based catalysts.⁶⁴ This approach proposes that the role of the metal is to facilitate the incorporation of nitrogen into the carbon matrix, increasing the ORR active site density on the catalysts. Through XPS characterization, only pyridinic-N, quaternary-N and pyridine-N-oxide were identified after 800 °C pyrolysis. However, XPS results after stability revealed a dramatic decrease of the intensity of the pyridinic-N peak and

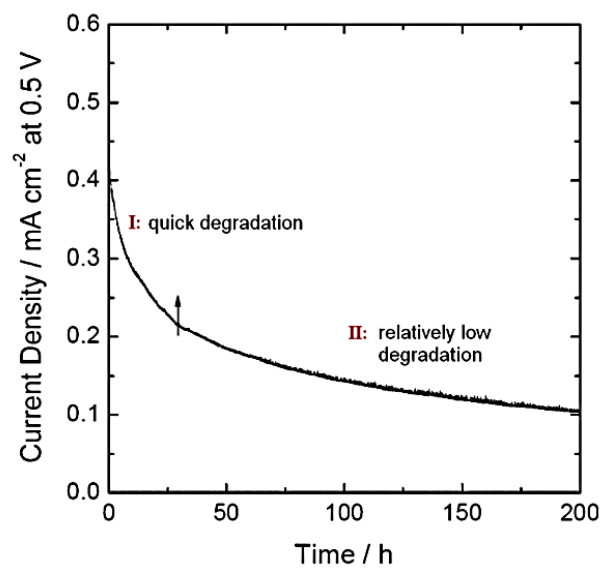
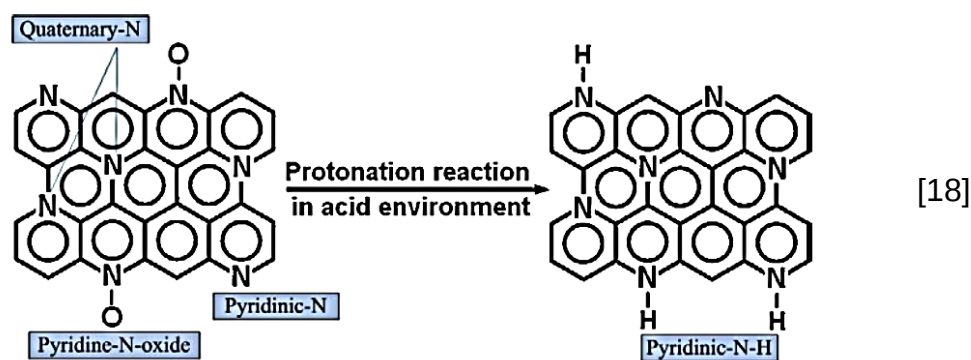


Figure 5. A typical plot of the current density at 0.5 V as a function of time for an H₂-O₂ fuel cell using nitrogen-modified carbon-based catalyst as cathode catalyst.

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the disappearance of the pyridine-N-oxide peak. This outcome, which was only observed in acidic medium, led to the hypothesis that protonation (equation [18]) of the lone pair of electrons on the pyridinic-N and pyridine-N-oxide can contribute to the loss of ORR activity during PEMFC operation.^{80,117} The quaternary- or graphitic-N, which does not possess lone pair electrons, is considered less susceptible to protonation and, therefore, more stable. This trend was observed when the sample synthesized in the same way was pyrolyzed at 1000 °C, exhibiting a higher graphitic-N content, and a higher stability than the sample heat treated at 800 °C.



The XPS technique, however, does not allow the differentiation between pyridinic-N-H and quaternary-N, which hinders the confirmation of this hypothesis.¹¹⁹ Furthermore, RDE results showed superior performance with the catalyst heat-treated at lower temperature (800°C).¹¹⁸ This result does not agree with the degradation mechanism proposed, which would predict a dramatic performance

loss, and, therefore, comparable RDE results for the heat-treated catalysts at the highly acidic RDE conditions.

Dodelet's group, on the other hand, proposed a variation of the protonation mechanism.¹⁰² First, this mechanism works under the widely accepted premise that FeN₂/C and FeN₄/C correspond to the active sites.^{9,120} This premise has been supported by Time-of-Flight Secondary ion Mass Spectrometry (ToF SIMS) experiments with perylene tetracarboxylic dianhydride (PTCDA) as a carbon precursor and different Fe precursors (Fe acetate and FeTMPP-Cl) and Fe contents (0.2 or 2.0 wt %) prepared by a two- step pyrolysis procedure.¹²⁰ This characterization showed a good correlation between catalytic activity and FeN₂/C abundance in all cases (results with the Fe acetate precursor are shown in Figure 6).

Secondly, Dodelet's mechanism proposes the protonation of ORR inactive N-groups with a subsequent anion adsorption, which is what ultimately is expected to cause the catalyst deactivation.¹⁰² This hypothesis sought to explain the stability results obtained with Fe/N/C catalysts prepared with a pyrolysis in NH₃ under three different conditions: holding the voltage at (1) OCV (OCV-mode), and (2) 0.5 V under H₂/O₂ and (3) 0.5 V under H₂/N₂, for 100 h while taking activity measurements at various times. As expected, the 0.5 V-mode (H₂/O₂) exhibited the highest performance loss (~5x) when compared with the OCV-mode and the 0.5 V-mode (H₂/N₂). However, the fact that these modes (OCV-mode and the 0.5

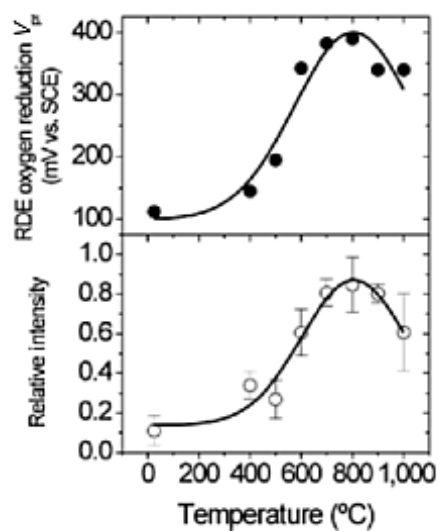
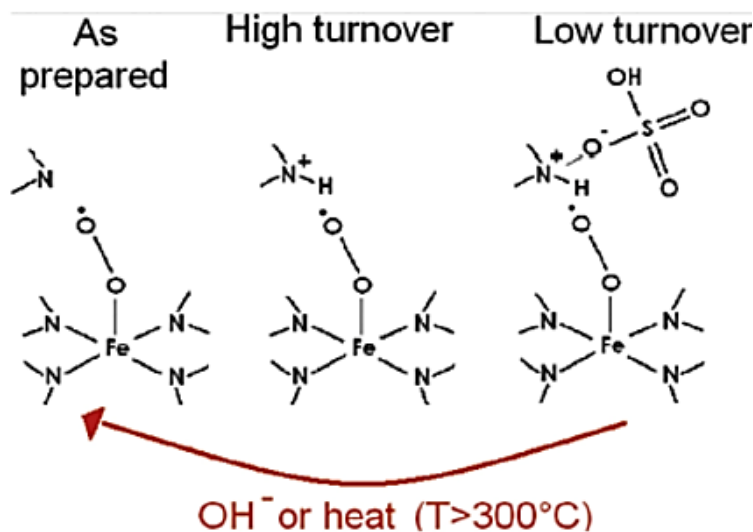


Figure 6. Comparison between changes with the pyrolysis temperature of the catalyst activity (top panel) and the relative intensity of FeN_2C_y^+ (bottom panel), measured in catalysts obtained by adsorbing acetate (0.2 wt % Fe) on prepyrolyzed PTCDA and heat treating the material in inert atmosphere at various temperatures, ranging from 400 to 1000 °C. ¹²⁰

V- mode (H_2/N_2)) suffered a performance loss despite the minimal ORR Faradaic charge (which also implies low H_2O_2 production), suggests the existence of an additional degradation mechanism.

Further exploration of this phenomenon involved soaking the original (O) catalyst in pH 1 H_2SO_4 (labeled as AW or “acid washed” catalyst) for 100 h and a subsequent heat treatment in argon (labeled as RHT or “reheat-treated” catalysts). Experiments with the AW catalyst showed a ~20 times lower initial activity than that exhibited by the O catalyst and equal to that obtained after 50 h under OCV-mode. Based on this, they concluded that the activity-decay mechanism during OCV-mode can be related to that during acid washing. Furthermore, the RHT catalyst evinced a 50% recovery of the initial catalytic performance. Based on thermogravimetric analysis and mass spectroscopy, this recovery was associated to the removal of HSO_4^- anions from the catalytic surface. Mössbauer spectroscopy discarded the possibility that this adsorption could take place on the active sites. Therefore, the suggested mechanism proposes that anion adsorption occurs on N-functional groups which are easily protonated at a pH ~1. This hypothesis was further confirmed by the performance recovery observed after washing the AW catalyst in NaOH. Equation [19] shows a depiction of this mechanism.



[19]

This dramatic decrease in catalytic activity after acid washing reported by Herranz et al.,¹⁰² however, does not concur with the results obtained by Schulenburg et al.¹¹¹ in 2003. In the latter study, which was discussed above in the context of the H_2O_2 mechanism, the acid treatment effect on the catalytic activity of carbon-supported FeTMPP-Cl was investigated. After mixing the catalyst with a 0.5 M H_2SO_4 solution for 100 h, no significant change in the catalytic activity of the material was observed. Since no signal of metallic Fe was observed in the Mössbauer spectrum after acid washing, it was determined that metallic Fe was not active towards the ORR.

3.1.2.4 Micropore Flooding

Several studies by Dodelet's group have suggested that PGM-free active sites reside within micropores.^{88,121} This hypothesis has emerged from their study on

the effects of time and temperature of heat treatment on Fe-based catalysts activity. By the structural and electrochemical characterization of a series of Fe-based materials with various heat-treatment times, a correlation between the surface area imparted by micropores and the activity towards the ORR was found (Figure 7). This observation promoted the idea that the catalytic site can be a molecular assembly bridging two pore walls, and therefore, a specific interpore distance is required for the site to be formed. Ferrandon et al. found a similar trend (direct microporous surface area-ORR activity proportionality) with a heat-treated PANI-Fe-C study at various temperatures.¹²² The highest ORR activity was obtained with the catalyst heated at 900 °C, which also corresponded to the largest Fe-N_x content as determined by X-ray absorption near-edge structure (XANES) measurements using linear combination fitting.

This observation has led to the conclusion that water flooding in the micropores can drastically accentuate mass transport limitations in the PEMFC cathode.^{87,95,103,123} A recent study, however, has contradicted this hypothesis through *in situ* CV experiments.⁹⁴ In this study, double layer capacitance (C_{DL}) measurements were interpreted as a function of the electrochemically accessible surface area (equation [20]), which is, in turn, interpreted as a measure of the degree of micropore wetting.

$$C_{DL} = \frac{\varepsilon \varepsilon_0 E C S A}{d} \quad [20]$$

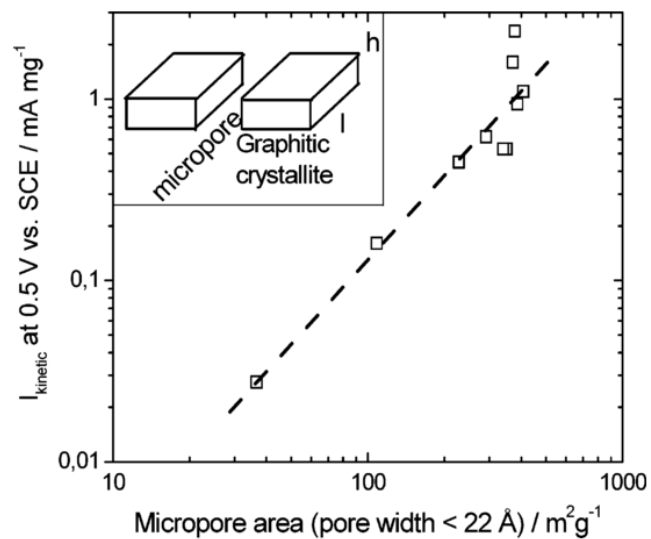


Figure 7. Activity for the O₂ reduction vs BET microporous area of catalysts obtained by adsorbing acetate (0.2 wt % Fe) on carbon black and heat treating the material in NH₃ at 900 °C for 20 mins.¹²¹

However, no significant change was observed from the capacitance calculations before and after air and O₂ polarization curves at 60% and 100 % RH. Specific capacitance calculations suggested that the majority of the micropores were wetted at the beginning of life. Furthermore, analysis of the polarization curves over time revealed predominance of kinetic losses over mass transport losses.

3..1.3 PGM-free Cathode Catalyst Layer

As illustrated in the previous discussion, attention mainly has been focused on the evaluation of PGM-free catalyst activity via RDE and RRDE studies. This approach facilitates the kinetic study of interfacial processes by guaranteeing a thorough control of the convection and diffusion processes of reactant and product to and from the electrode.¹²⁴ However, RDE results do not depict a realistic perspective of PGM-free catalyst behavior in a PEMFC environment, where phenomena such as mass transport, membrane degradation and the complex interplay between catalyst and ionomer can influence the overall catalytic performance. Few studies have focused on the integration of promising PGM-free catalysts into the PEMFC cathode and the optimization of the PGM-free electrode macroscopic properties. To achieve the performance targets ($0.044\text{A}\cdot\text{cm}^{-2}$ at 0.9V) established by the US DOE, advances in catalyst layer development are necessary. Understanding and optimizing relative losses due to kinetics versus mass transport is of importance considering that typical PGM-free catalyst layer thicknesses are significantly

higher (~10x) than their Pt-based catalyst counterparts and the number and intrinsic catalytic activity (e.g. turnover number) of active sites is also unknown. Recently, significant contributions exploring PGM-free cathode CLs have been published by different research groups.^{95,125–128} Olson et al. reported a detailed study of the effect on performance of parameters such as CL thickness and composition in electrodes in FCs.¹²⁶ Through a ΔE vs. i analysis on a cobalt-based cathode catalyst, they found that transport limitations were appreciable even at relatively low-current density. The non-platinum CL in Olson's study includes the addition of polytetrafluoroethylene (PTFE)-supported carbon (PTFE/C) composite powder.¹²⁶

Multiple studies have reported a significant influence of ionomer content on the PGM-free cathode performance.^{128,129} Serov et al. showed a proportional correlation between PEMFC performance and ionomer content of Fe-containing nicarbazin-derived cathode at 100% RH and 1 bar O₂ partial pressure.¹²⁹ Increasing the ionomer content from 35 to 55% Nafion resulted in higher kinetic current. Stariha et al., on the other hand, found that optimal performance of the Fe-N-C cathode catalysts in air was obtained with 35 wt% Nafion.¹²⁸ Optimal ionomer content, therefore, is influenced by the catalyst material structure and a high ionomer content can result in a trade-off between kinetic and mass-transport effects at high current density values.

Recently, Banham et al. reported a significant improvement of fuel cell performance, reaching a current density of $0.044 \text{ A}\cdot\text{cm}^{-2}$ at $\sim 880 \text{ mV}$ with a precommercial microporous ($>90\%$) Fe-based catalyst (35% ionomer content).⁹⁵ This publication indicates a significant influence of the PGM-free cathode CL loading on the overall PEMFC performance based on a polarization analysis with different cathode loadings (1, 2.5 and $4 \text{ mg}\cdot\text{cm}^{-2}$) and a 40 wt% Nafion. Higher cathode loadings showed significant mass transport limitations at high current densities, while low loadings exhibited higher kinetic losses in the low current regime. To reduce the mass transport effect in the $4 \text{ mg}\cdot\text{cm}^{-2}$ cathode, the ionomer content was decreased from 40 wt% to 35 wt%, resulting in a performance gain over the whole current density range. Furthermore, the stability was found to be directly proportional to the cathode CL loading. This trend along with the non-uniform increase in C_{DL} observed by CV characterization before and after stability tests, led to the conclusion that the degradation of the PGM-free cathode catalysts was likely occurring through oxidation of the catalyst surface. Increasing the PGM-free cathode loading, however, can lead to additional issues related to the cathode CL quality, such as cracking or flaking during PEMFC operation, setting a limitation to this approach.

3..1.4 Summary

As illustrated in the previous discussion, important advances in performance have been achieved with PGM-free catalysts in terms of catalytic activity and durability.

Achieving commercial performance requirements, however, requires a better understanding of the morphology and structure of these materials and their properties when integrated in a PEMFC cathode.

In the present contribution, we study the ORR activity of the CHF-1 catalyst described above after pyrolysis at 700°C under inert atmosphere. RDE and RRDE experiments are performed to determine the onset potential and number of electrons transferred. The structure and properties of the material are characterized using TEM, SEM, XRD and surface area analysis. Furthermore, this paper proposes a methodology for PGM-free catalyst evaluation in low temperature FCs under realistic operation conditions, and identification of the individual voltage loss contributions.

3.2 Heat-Treatment Temperature Effect

The activity, in terms of the ORR onset and half-wave potentials in the RDE plots, undergoes a significant increase after the sample was heat-activated under nitrogen atmosphere at temperatures up to 700°C and then drops for the material pyrolyzed at higher temperatures(800-1000°C), as shown in Figure 8. An optimal performance was achieved for the sample pyrolyzed at a temperature of 700°C with an onset potential of 0.87 V.

The best-performing CHF-1(Fe) sample, heat treated at 700°C, exhibits the lowest hydrogen peroxide yield over the potential range from -0.2 to 0.9 V

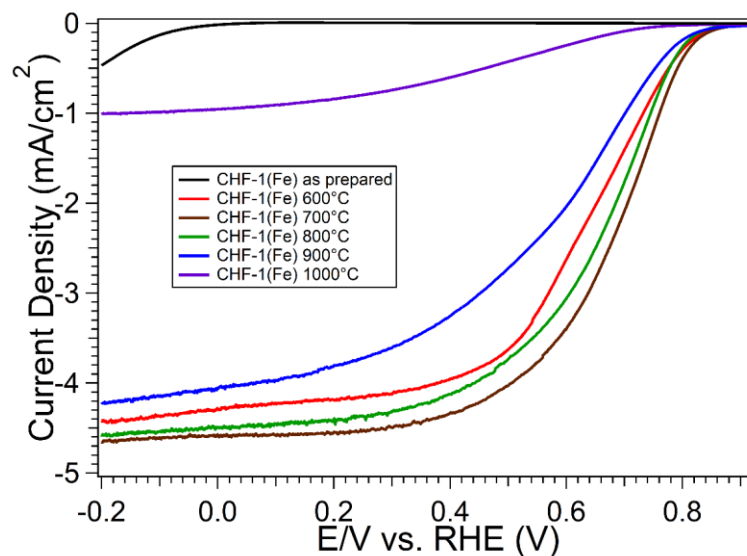


Figure 8. RDE curves for the untreated and pre-treated iron porphyrin framework at different heat-treatment temperatures (600-1000°C). 1600 rpm, $10 \text{ mV}\cdot\text{s}^{-1}$ scan rate, room temperature, 0.1 M H_2SO_4 electrolyte, $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode and Au wire counter electrode.

(Figure 9). This suggests that the oxygen reduction reaction is mainly proceeding through an overall four-electron transfer path: either by the direct four-electron oxygen reduction or by the two-electron reduction to produce hydrogen peroxide and its subsequent oxidation. Hydrogen peroxide yields for the heat-treated material are comparable to that of Pt-based catalysts (5% H₂O₂ yield at 0.4 V for CHF-1(Fe) heat-treated at 700°C vs 3-4% H₂O₂ yield at 0.4 V on 14 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ Pt/C).

The 700°C pyrolyzed sample was, therefore, subjected to acid treatment and a second pyrolysis at the same temperature (700°C). All further characterization in this chapter was performed with the material resultant after these three stages (700°C/H₂SO₄/700°C), unless otherwise specified.

3.3 Physicochemical Characterization

TEM images of the treated CHF-1 catalyst (700°C/H₂SO₄/700°C) are presented in Figure 10. These images show the presence of Fe particles distributed throughout the carbon structure (Figure 10A). The average Fe particle size calculated from the images is 13 nm.

The presence of a shell of graphite can be observed (Figure 10B), as has been reported previously with FeTMPP-Cl pyrolyzed at 1000°C,¹³⁰ and PANI-derived electrocatalysts at 900°C.⁴⁴ Particles surrounded by graphitic shell exhibit a higher resistance to dissolution in acidic medium and therefore higher stability in the fuel

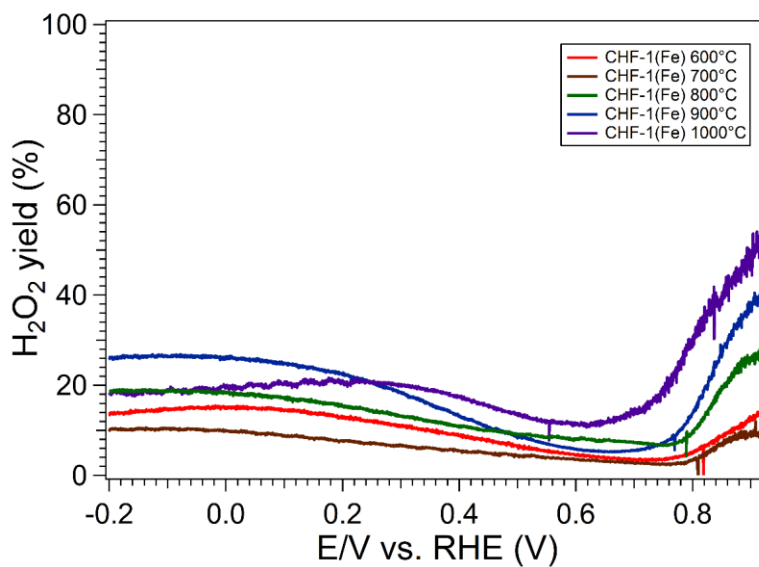


Figure 9. H₂O₂ yield plots measured for the pre-treated iron porphyrin framework at different heat-treatment temperatures (600-1000°C). 1600 rpm, 10 mV·s⁻¹ scan rate, room temperature, 0.1 M H₂SO₄ electrolyte, Hg/Hg₂SO₄ reference electrode and Au wire counter electrode.

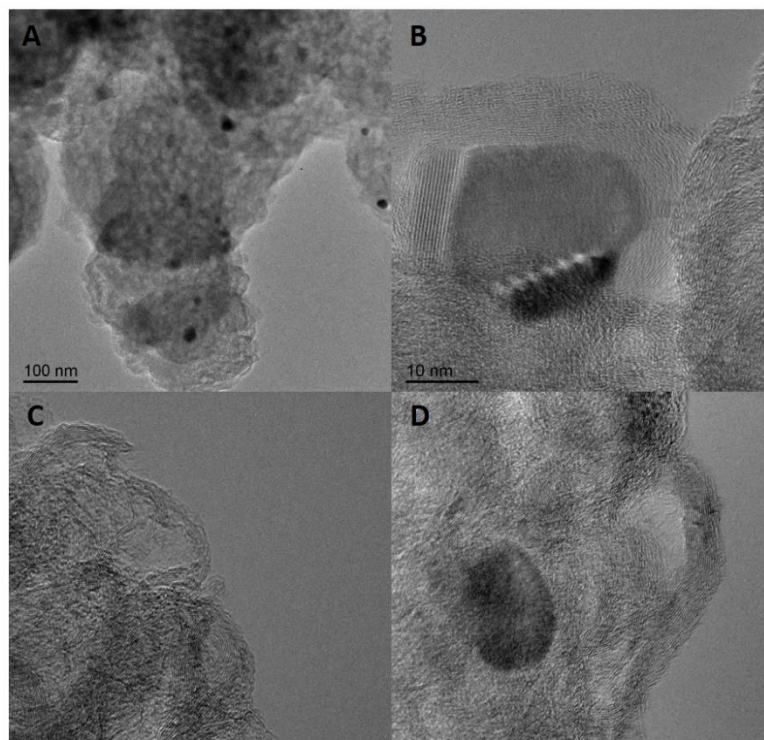


Figure 10. High-resolution (HR)TEM images of the 700°C pyrolyzed iron porphyrin framework-based catalyst (A) HRTEM image of the iron nanoparticle distribution on the catalyst structure. (B) HRTEM image showing an onion-like mesographitic nanoshell surrounding Fe particle. (C) HRTEM image showing the mesographitic structure of the carbon support. (D) HRTEM image of a typical non-precious metal catalyst nanostructure involving carbon and metal aggregates.

cell environment. The carbon structure observed by TEM imaging (Figure 10C, D) is defined as turbostratic or mesographitic, given that the basal planes are not well-aligned compared to an ideal fully graphitized carbon structure.

SEM images of the as-synthesized (Figure 11A, B), 700°C pyrolyzed (Figure 11C, D) and acid treated with a second 700°C heat treatment (Figure 11E, F) samples. The images A, C and E are the BSE images. As expected, the as-synthesized material (Figure 11A) does not exhibit metal particles formation, given that at this point the iron is embedded in the organic structure. However, in the heat-treated samples before (Figure 11 C) and after (Figure 11E) acid treatment, the Fe particles formed during the pyrolysis process are easily visualized (due to its higher atomic number). The particles show a uniform distribution throughout the sample, with the presence of few agglomerates, both before and after acid treatment. In agreement with previous observations by Ma et al.,⁸ the as-synthesized CHF-1 (Figure 11 A,B) structure is composed of agglomerated ball-shaped particles (200-400 nm diameter), exhibiting a high surface area and pore volume ($0.442 \text{ cm}^3 \cdot \text{g}^{-1}$), as confirmed through BET results (see Table 1). On the other hand, the samples after pyrolysis (Figure 11 C, D, E, F) exhibit more extensive agglomeration and a heterogeneous particle size distribution, which causes an evident decrease of the surface area and pore volume (Table 1). However, it is worth noting that the sample subjected to acid leaching (Figure 11 E, F), not only exhibits a lower density of

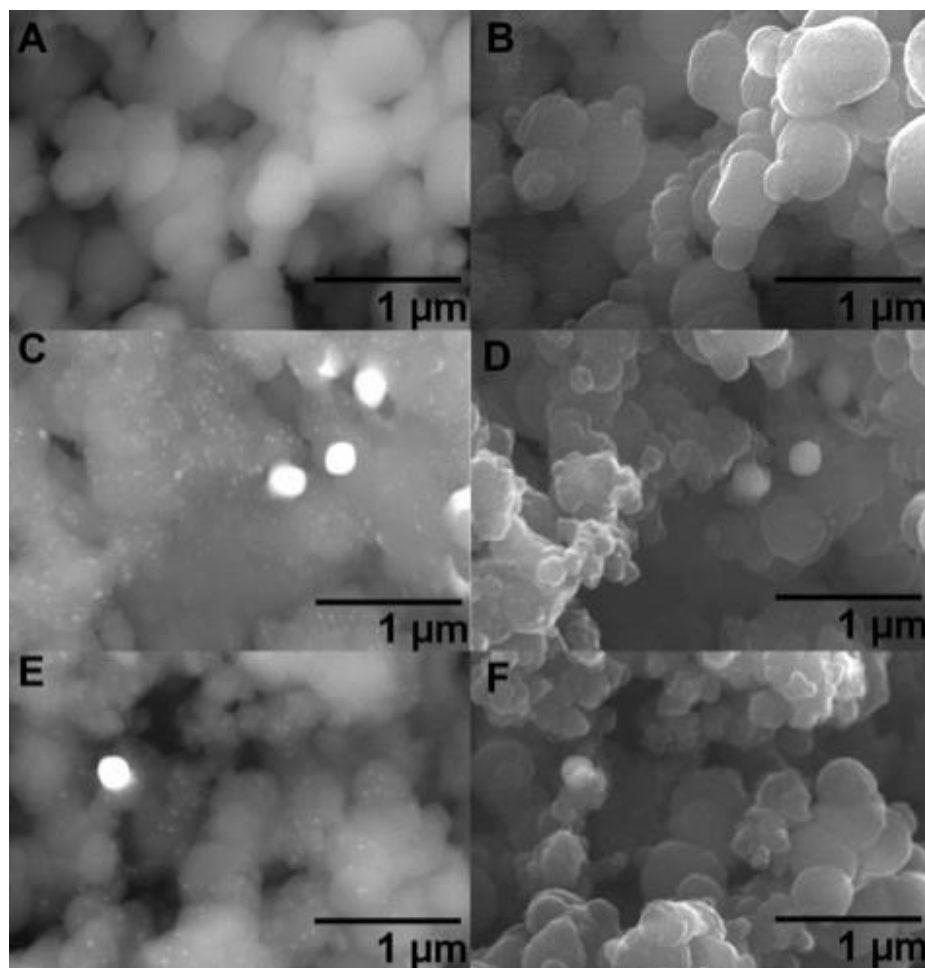


Figure 11. Back-scattered and secondary electron images of the highly porous as-synthesized (A, B), 700°C pyrolyzed (C, D) showing the presence of iron nanoparticles, and acid treated (E, F) CHF-1 catalyst. The latter exhibits a lower density of metal particles and a higher porosity (Table 2) as a result of the acid leaching process.

Table 1. BET measurements of material.

Material	BET Surface Area [m²·g⁻¹]	Pore Volume [cm³·g⁻¹]
CHF-1 (Fe) (As-prepared)	1526.326	0.442
CHF-1 (700°C)	288.883	0.100
CHF -1 (700°C + AT+ 700°C)	393.389	0.129

metallic particles, but a better-defined structure in terms of exposed area and porosity (Table 1).

The metal content was evaluated through ICP-OES and SEM-based energy dispersive X-ray spectroscopy (EDS) analysis (Table 2), showing a decrease of 50% in the Fe content after acid treatment. Differences in the composition measured with the two techniques can be related to the volume of material analyzed using the SEM-EDS technique, in comparison to ICP-OES, which is a bulk composition analysis technique.

The XRD patterns corresponding to the as-synthesized and pyrolyzed (before and after the acid treatment) samples are presented in Figure 12. The presence of graphitic carbon ($2\theta=26^\circ$) and metallic Fe (110) ($2\theta=45^\circ$) can be appreciated in both pyrolyzed samples (before and after acid treatment), in agreement with the observations made from TEM and SEM images.

3.4 Catalytic Activity: RRDE technique

Figure 13 shows the RDE plots for the as-synthesized and pyrolyzed (before and after acid treatment) samples (A) and the number of electrons transferred measured using RRDE with a Pt ring (B). From Figure 13A, it can be observed that the as-synthesized material does not show significant activity towards the ORR (-0.048 V onset potential). The samples subjected to heat treatment exhibit a significant improvement in catalytic activity with an onset potential of 0.868 V and

Table 2. Fe content of material before and after heat/acid treatment measured with ICP-OES and EDS.

Material	ICP-OES Fe Content (%)	EDS Fe Content (%)
CHF-1 (As-prepared)	5.64	11.82
CHF-1 (700°C/H₂SO₄/700°C)	3.84	5.73

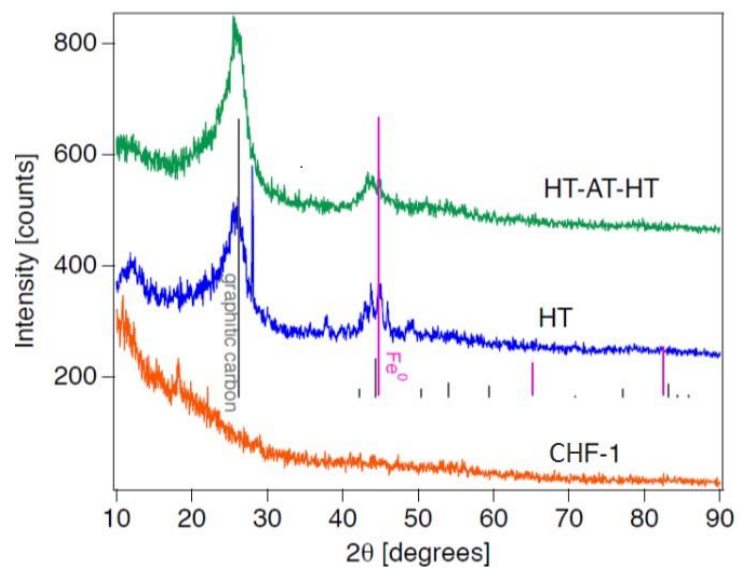


Figure 12. Cu K α x-ray diffraction patterns for the as-prepared catalyst (CHF-1), the catalyst after 700°C heat treatment (HT), and the catalyst after 700°C heat treatment followed by acid treatment and final 700°C heat treatment (HT+AT+HT).

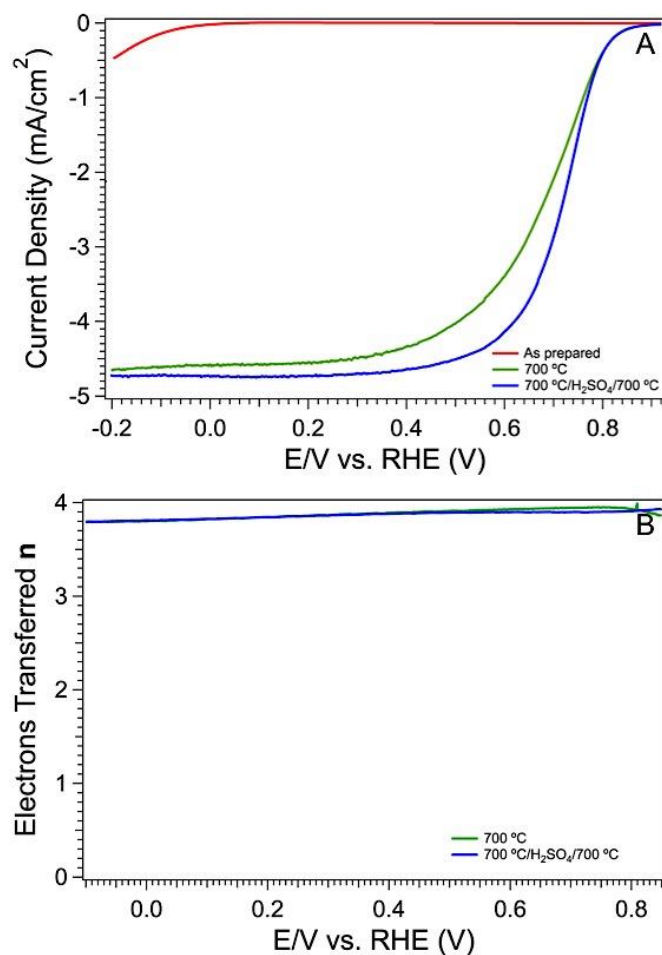


Figure 13. RDE curves for (A) the as-prepared and pre-treated CHF-1 (1600 rpm, 10 mV·s⁻¹ scan rate, 0.1 M H₂SO₄ electrolyte, Hg/Hg₂SO₄ reference electrode and Au wire counter electrode) and (B) number of electrons transferred for the pre-treated CHF-1 catalyst (Ring electrode kept at 1.2 V).

0.861 V (measured at the potential at which the current density reaches $50 \mu\text{A}\cdot\text{cm}^{-2}$) for the samples before and after acid treatment, respectively. This increase in the onset potential (compared to the as-prepared sample) has been correlated with the graphite shell formation (Figure 13B) in previous studies.¹³⁰ The acid-treated sample yielded a higher limiting current density. The higher current density could be explained by the removal of excess metallic particles that could potentially hinder the access of the reactants to the active sites (Table 2) or by the rearrangement of the catalyst structure through the second heat-treatment that can lead to the formation of new active sites.

The number of electrons transferred calculated through RRDE was 3.8 electrons in the limiting current region, as observed in Figure 13B for the pyrolyzed samples (before and after acid treatment), which implies that the peroxide production is approximately 10% of the product. This result suggests that the reaction is mainly proceeding through the four-electron transfer path.

When the oxygen partial pressure is varied, the current density on the RDE plots changes as a function of the oxygen partial pressure. As an example, plots for 20, 40, 60, 80 and 100% oxygen are shown in Figure 14. The inset plot shows the direct correlation between the oxygen partial pressure and the limiting current density.

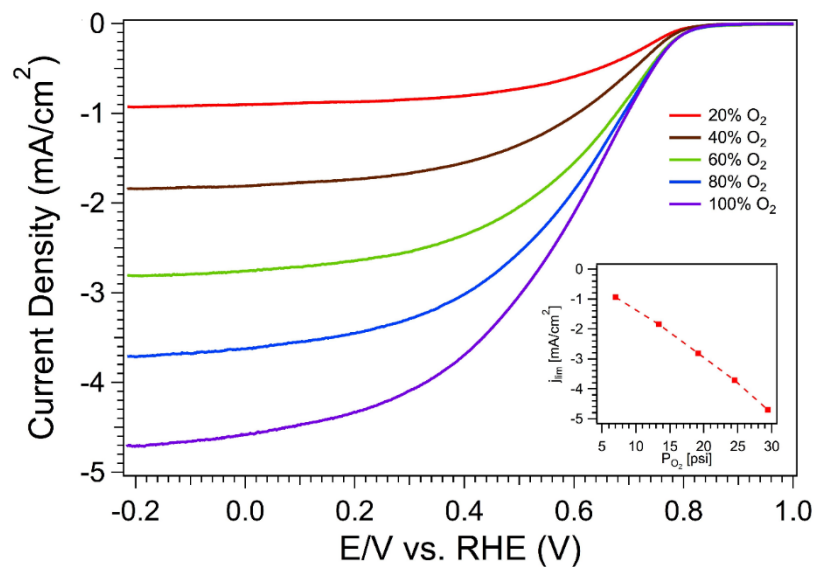


Figure 14. RDE curves for the pre-treated iron porphyrin framework at different oxygen partial pressures. 1600 rpm, 10 mV·s⁻¹ scan rate. 0.1 M H₂SO₄ electrolyte, Hg/Hg₂SO₄ reference electrode and Au wire counter electrode.

3.5 Catalyst Layer Nafion Content

The highest Nafion to catalyst ratio (70:30) ink presented agglomeration issues, which prevented a suitable electrode preparation and subsequent fuel cell testing. The results obtained with the 30:70 and 50:50 Nafion to catalyst ratios are shown in Figure 15. Although both ratios exhibit a similar behavior at high voltages, the 50:50 Nafion to CHF-1 electrode undergoes a more significant drop at lower voltages. The current density for the 30:70 CHF-1 to Nafion electrode, at 0.4 V, is 40% higher than for the 50:50 CHF-1 to Nafion electrode. This could be related to a higher extent of ionomer agglomeration, which affects the global structure of the electrode. Therefore, further FC characterization was performed with a 30:70 Nafion to catalyst ratio.

3.6 Fuel Cell Testing

The iR_{Ω} -free polarization and resistance curves obtained from MEAs comprising iron porphyrin framework-based cathodes with different catalyst loadings ($1 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$, $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ and $3 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$) are shown in Figure 16. The current density, which is relatively low ($\leq 2 \cdot 10^{-5} \text{ A cm}^{-2}$) above 0.7 V, increases to ca. 0.10 A cm^{-2} at 0.6 V for all loadings. The maximum power density for $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ is 0.46 W cm^{-2} , for $1 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ catalyst loading is 0.32 W cm^{-2} compared with 0.22 W cm^{-2} for $3 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$, suggesting a significant influence of the CL loading on the

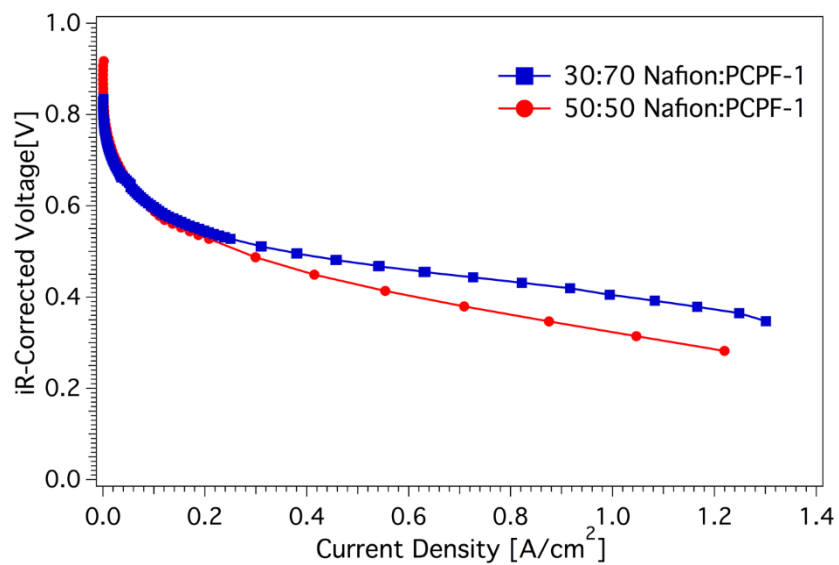


Figure 15. Polarization and resistance curves for H₂-O₂ PEM fuel cells with a 2 mg_{cat}·cm⁻² cathode catalyst loading and different catalyst to Nafion ratios (30:70 and 50:50). The curves were obtained with inlet gases heated and humidified to 83 °C, 2 atm backpressure.

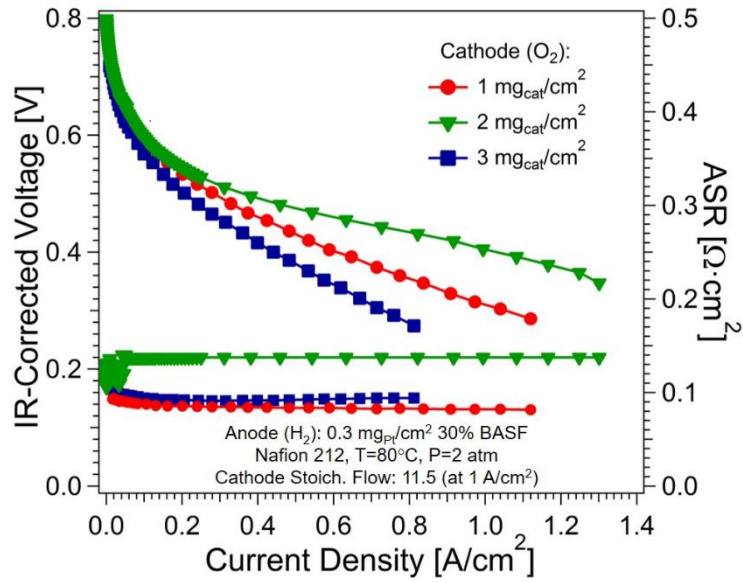


Figure 16. Polarization and resistance curves for $\text{H}_2\text{-O}_2$ PEMFCs with different cathode catalyst loadings: $1 \text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$ (—●—), $2 \text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$ (—▼—) and $3 \text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$ (—■—). The curves were obtained with inlet gases heated and humidified to 83°C , 2 atm backpressure and the cell temperature was held at 80°C .

performance of the PEMFC. A loading of $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ provided the best results in terms of FC performance. This data, obtained at 100% O_2 , gives a first glimpse of the behavior of this system. The polarization curves, showing the stability of the material through cycling according to the testing protocol described, are shown in Figure 17. A significant performance loss is observed over the entire voltage range, approximately $0.37 \text{ A} \cdot \text{cm}^{-2}$ was observed at 0.4 V after 49 cycles (~ 49 hours).

To provide data for a more extensive analysis, we probe the influence of oxygen partial pressure variations on the performance of the material, shown for $3 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ loading in Figure 18. This data is typical of all loadings. Significant decrease in current density obtained at a given cell voltage is observed in most regions of the polarization curve. To further interpret these results, we must analyze both kinetics and mass transport aspects revealed by the data.

3.7 Electrochemical Impedance Spectroscopy (EIS)

The measured impedance responses for each oxygen pressure are shown Figure 19 for a set of voltages throughout the Tafel region. At higher oxygen pressures (20% and up), the typical high voltage pattern of the EI spectra is observed: a single depressed semicircle with diameter R_p , which decreases with voltage).^{131,132} As seen from the Bode plots presented in Figure 20, the characteristic frequencies of this loop increase with decreasing potential and increasing oxygen concentration.

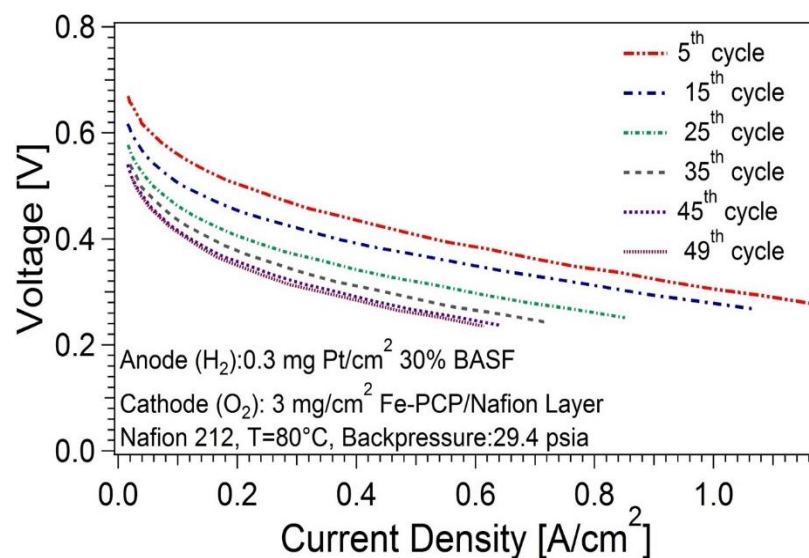


Figure 17. Polarization curves for $\text{H}_2\text{-O}_2$ PEM fuel cells with $3 \text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$ catalyst loading after constant cycling. The curves were obtained with inlet gases heated and humidified to 83°C , 2 atm backpressure and the cell temperature was held at 80°C .

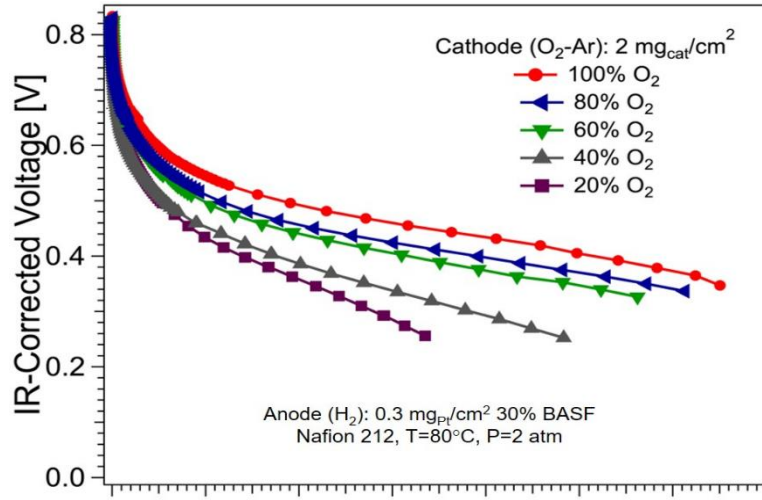


Figure 18. Polarization curves for PEMFCs with 2 mg_{cat}·cm⁻² cathode catalyst loading and oxygen partial pressure variation: 20% O₂ (SF: 2.8), 40% O₂ (SF: 5.2), 60% O₂ (SF: 7.5), 80% O₂ (SF: 9.5) and 100% O₂ (SF: 11.5). The curves were obtained with inlet gases heated and humidified to 83 °C, 2 atm backpressure and the cell temperature was held at 80°C. (SF: Cathode Stoichiometric Flow at 1 A·cm⁻²).

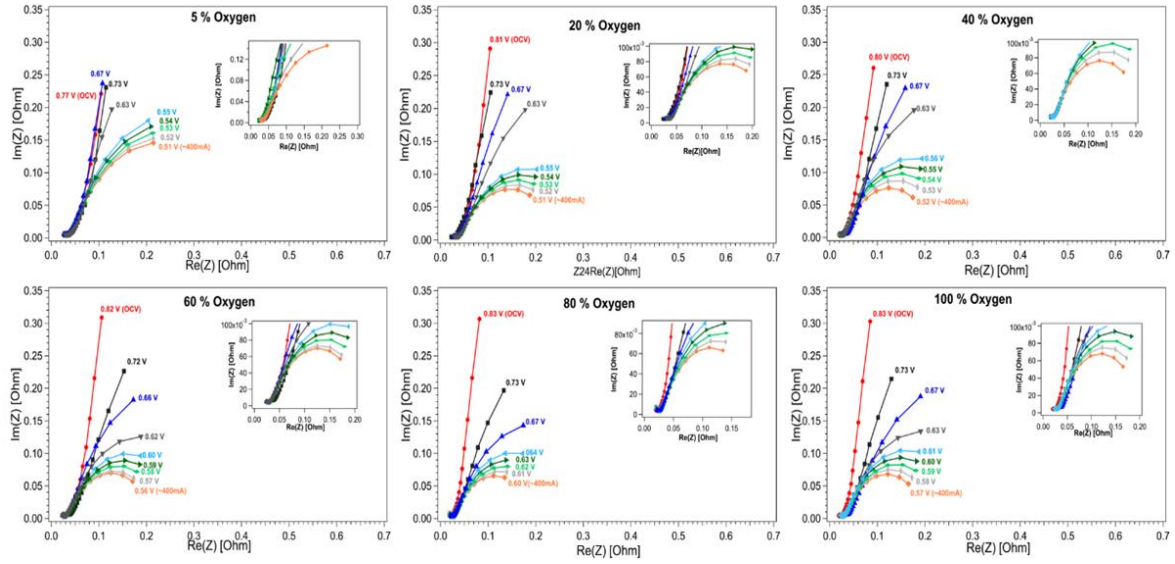


Figure 19. Measured impedance response for PEM fuel cell with $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ cathode catalyst loading and oxygen partial pressure variation. Plots at different voltage values are shown for each oxygen pressure.

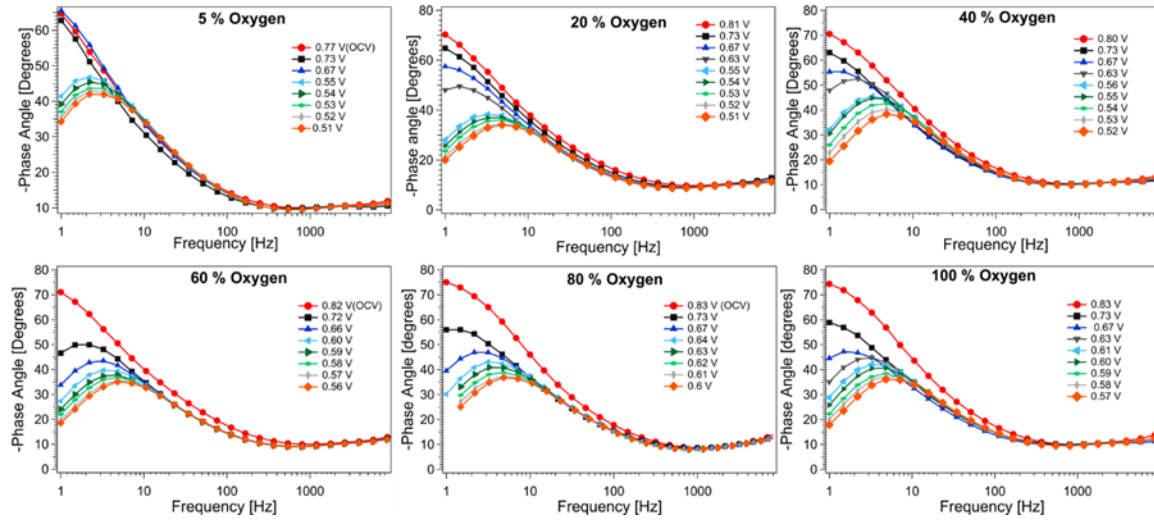


Figure 20. Bode plots response for PEM fuel cell with $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ cathode catalyst loading and oxygen partial pressure variation. Plots at different voltage values are shown for each oxygen pressure.

Given the absence of a second (low-frequency) semicircle or any sign of concavity change of the first loop, R_p could be associated with the charge transfer across the catalyst-electrolyte interface.¹³³ An equivalent circuit (Figure 21) taking into account the ohmic and contact resistance (R_Ω) of the electrochemical cell, a constant phase element T_1 , which accounts for the effect of the porous electrode on the double-layer capacitance and the charge transfer resistance R_1 . Fitting of the impedance plots was carried out to calculate the parameter values (T_1 , R_1 and R_Ω) as shown in Figure 21 for the $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ cathode catalyst loading at 100% oxygen partial pressure and 0.6 V. The calculated values are shown in Table 3 for each oxygen pressure.

To be able to determine if there are other contributions, the cathode potential (iR-corrected cell voltage) was represented as a function of $\log R_p^{-1}$ (Figure 22). The linear relationship between the cathode potential (E_{cath}) and $\log R_p^{-1}$ can be associated to a Tafel plot, where charge transfer represents the main contribution to R_p :

$$E_{\text{cath}} = E_o - b \log R_p^{-1} \quad [21]$$

where $b = 2.3b'$ ($b' = RT/\alpha nF$). In Figure 22 the values of b calculated from the different plots have been included. In general terms, the plots corresponding to higher oxygen pressures present a good fitting to a linear behavior. Lower oxygen

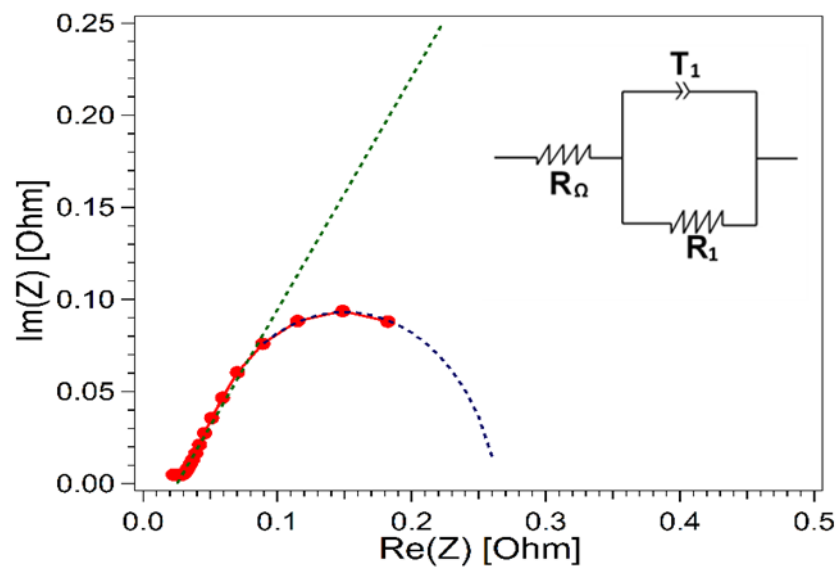


Figure 21. Measured Impedance response for PEM fuel cell with $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ cathode catalyst loading at 100% oxygen partial pressure and 0.6 V, semicircle and CPE fitting included.

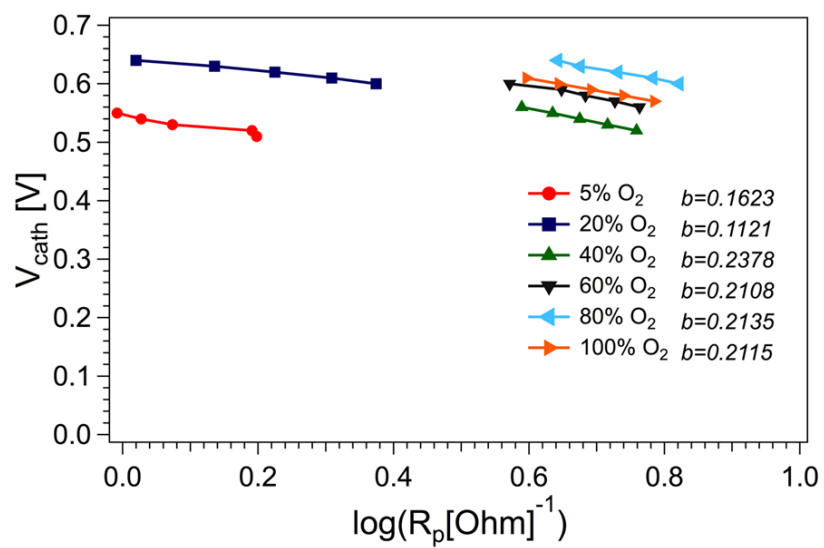


Figure 22. Cathode potential as a function of $\log(R_p^{-1})$ at different oxygen pressures.

Table 3. Charge transfer resistance and CPE calculations.

O₂ Partial Pressure	100%	Voltage [V]	0.57	0.58	0.59	0.6	0.61
		R _Ω [Ω]	0.2009	0.2196	0.2416	0.2639	0.2918
		R ₁ [Ω]	0.1641	0.1822	0.2033	0.2270	0.2534
		T ₁	0.0207	0.0291	0.0272	0.0207	0.0368
	80%	Voltage [V]	0.60	0.61	0.62	0.63	0.64
		R _Ω [Ω]	0.1837	0.2006	0.2225	0.2440	0.2630
		R ₁ [Ω]	0.1508	0.1649	0.1857	0.2110	0.2279
		T ₁	0.0360	0.0354	0.0363	0.0348	0.0309
	60%	Voltage [V]	0.56	0.57	0.58	0.59	0.60
		R _Ω [Ω]	0.2126	0.2289	0.2501	0.2683	0.3075
		R ₁ [Ω]	0.1725	0.1876	0.2073	0.2250	0.2683
		T ₁	0.0283	0.0347	0.0385	0.0472	0.0178
	40%	Voltage [V]	0.52	0.53	0.54	0.55	0.56
		R _Ω [Ω]	0.2134	0.2317	0.2509	0.2710	0.2977
		R ₁ [Ω]	0.13	0.1923	0.2114	0.2319	0.2575
		T ₁	0.0342	0.0362	0.0313	0.0479	0.0430
	20%	Voltage [V]	0.60	0.61	0.62	0.63	0.64
		R _Ω [Ω]	0.4817	0.5494	0.6507	0.7843	1.0060
		R ₁ [Ω]	0.4224	0.4912	0.5959	0.7318	0.9560
		T ₁	0.0238	0.0923	0.0873	0.0476	0.0443
	5%	Voltage [V]	0.51	0.52	0.53	0.54	0.55
		R _Ω [Ω]	0.6810	0.6954	0.8884	0.9846	1.0660
		R ₁ [Ω]	0.6341	0.6442	0.8443	0.9390	1.0192
		T ₁	0.07	0.0454	0.0268	0.0224	0.0395

concentrations (5-20%) show a larger deviation from the linear behavior, which can be associated with the larger mass transport contribution.

3.8 Individual Contributions Analysis

Given that the mass transport and proton conduction contributions in the low current region were found to be negligible based on the impedance analysis, the iR_{Ω} -free polarization curves acquired with different catalyst loadings and oxygen partial pressure were analyzed using the Tafel equation (Eqn. [22]).

$$\eta_{act} = a + b \log(i) \quad [22]$$

Where,

$$a = \frac{2.3RT}{\alpha F} \log(i_0) \text{ and } b = -\frac{2.3RT}{\alpha F} \quad [23]$$

Where η_{act} is the activation overpotential associated mainly with the sluggish O_2 reduction reaction kinetics, a and b are the Tafel parameters, i_0 is the exchange current, α is the cathodic transfer coefficient, R is the gas constant, F is the Faraday constant and T is the cell temperature.

Taking a and b as free parameters, least squares fitting was applied to find the best fits of equation [22] to the polarization curves at the Tafel region (i.e. low current densities $<0.1A \cdot cm^{-2}$). A representative curve acquired with the best-performing loading and a 100% oxygen partial pressure is shown in Figure 23. In

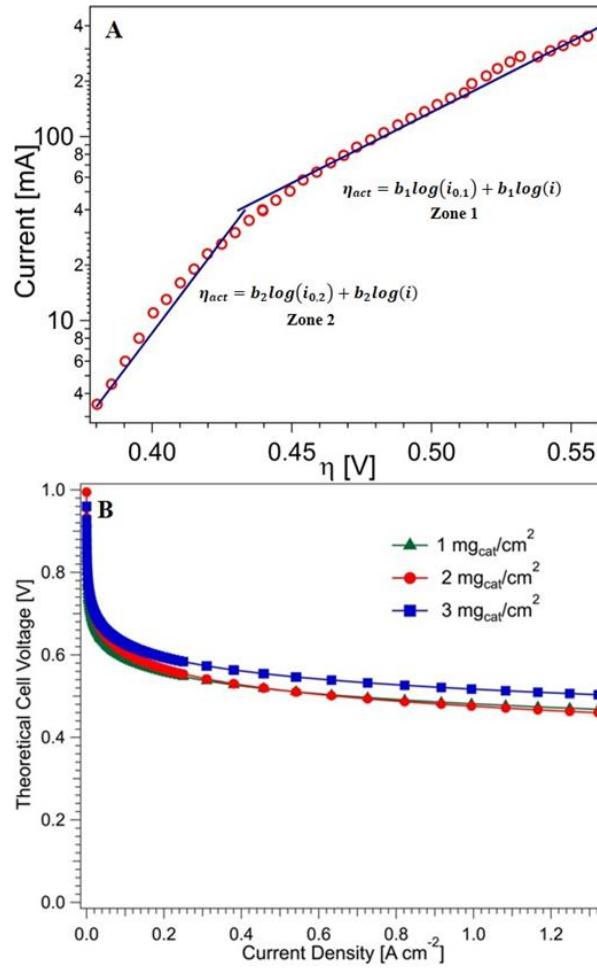


Figure 23. (A) iR_{Ω} -corrected Tafel plot of an MEA with 2 $mg_{cat} \cdot cm^{-2}$ PCPF-1 cathode and 0.2 $mg_{Pt} \cdot cm^{-2}$ anode with a cathode feeding of 100% oxygen (markers) and fit to the Tafel equation (line) (B) Theoretical polarization curves free of ohmic and mass transport losses.

all cases, two regimes were observed. For low cell voltages ('Zone 1', $\eta > 0.45\text{ V}$ i.e. $E_{cell} < 0.7\text{ V}$), the average Tafel slope is high ($118.0 \pm 8.9\text{ mV} \cdot \text{decade}^{-1}$), and at high cell voltages ('Zone 2', $\eta \leq 0.45$ i.e. $E_{cell} > 0.7\text{ V}$) the average Tafel slope is lower ($53.6 \pm 8.2\text{ mV} \cdot \text{decade}^{-1}$). Table 4 contains the parameters obtained from the fits for all curves. Unlike the case of Pt or Pt alloy catalysts, in which two Tafel slopes are also observed, it is unlikely that the kinetics is affected by the formation of oxides or other surface reactions in different potential regimes. We speculate that the presence of these two well-defined regimes could be related to the interaction with two different types of catalytic active sites (perhaps Fe-N₄/C and Fe-N₂/C^{9,120}). The presence of these two types of sites has been suggested in cases where an Fe and N precursor are simultaneously present in the pyrolysis process.^{9,120} We also note that the two types of catalyst sites would then have radically different intrinsic rates based on expected values of i_0 . At this point, we forgo a more detailed interpretation given the difficulties of exactly estimating this parameter for ORR via an unknown reaction. The parameters obtained at the low cell voltage range (Zone 1) were employed in the subsequent analysis.

Table 4. Tafel Parameters obtained for PEM fuel cells with different catalyst loadings ($1 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$, $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ and $3 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$) and oxygen partial pressure variation.

Loading [$\text{mg} \cdot \text{cm}^{-2}$]	P_{O_2}	b_1 [$\text{mV} \cdot \text{dec}^{-1}$]	$i_{0,1} \times 10^4$ [mA]	b_2 [$\text{mV} \cdot \text{dec}^{-1}$]	$i_{0,2} \times 10^8$ [mA]
1	20%	-119.04	7.96	-67.96	95.07
	40%	-119.32	17.39	-62.32	60.59
	60%	-125.19	30.22	-65.97	147.66
	80%	-115.23	22.75	-50.22	3.21
	100%	-109.32	20.19	-50.39	5.13
2	20%	-123.15	42.23	-62.97	143.75
	40%	-121.96	32.09	-49.82	1.75
	60%	-127.47	92.56	-56.55	49.42
	80%	-129.79	190.44	-49.68	7.58
	100%	-126.06	88.85	-57.17	48.39
3	20%	-122.25	57.69	-52.39	18.48
	40%	-114.10	33.72	-44.29	0.76
	60%	-95.23	9.10	-42.50	0.72
	80%	-111.50	41.48	-44.30	1.46
	100%	-110.79	51.40	-47.59	12.80

Using these parameters to extrapolate the Tafel behavior over the entire current regime, we obtain an approximation of the ‘kinetics-only’ cell performance in the absence of both ohmic and mass transport overpotential (Figure 23B). From the calculated polarization curves obtained for the different cathode catalyst loadings (Figure 23B) a direct correlation is observed between the cathode catalyst loading and the resulting kinetic performance. This agrees with the expectation that a higher cathode catalyst loading would imply a higher quantity of available active sites for the reaction to take place. However, the real performance exhibits a different trend, indicating that the ohmic and mass transport contributions have a strong influence on the overall performance. To study these effects in more detail, the individual contributions of these effects were calculated.

To identify the individual voltage loss contributions, the cell voltage can be broken down in terms of the individual overpotential contributions:

$$E_{cell} = E_{rev}(p_{H_2}, p_{O_2}, 80^\circ C) - \eta_{act} - \eta_{ohm} - \eta_{mt} \quad [24]$$

Where E_{rev} is the reversible OCV, η_{ohm} is the overpotential due to ohmic losses caused by electronic contact resistances between the flow-fields and the diffusion media and ohmic resistance due to proton conduction through the membrane ³⁴, and η_{mt} is the concentration overpotential, associated to the transport of O₂ through the diffusion medium and the CL. As shown previously, η_{act} can be estimated through extrapolation of the Tafel equation. η_{ohm} was determined by

multiplying the measured high-frequency resistance of the cell by the current density. In situ measured ohmic resistances for the different cells were approximately $0.25 \pm 0.06 \Omega\text{cm}^2$, which is an order of magnitude higher than measurements for standard Pt supported on carbon cathode catalyst ³⁴, and can be related to a lower intrinsic conductivity of the cathode material. Higher metal content and degree of graphitization in the cathode material, along with improved membrane conductivity and contact resistances between flow- fields and diffusion media, could contribute to the reduction of the overall voltage decline with increasing current density in the fuel cell performance for future designs.

The dashed line in Figure 24(A, B and C) corresponds to the calculated polarization curves free of ohmic and mass transport losses for each cathode loading, shown previously in Figure 23B. From these plots, we confirm that the activation overpotential accounts for most of the losses in the cell, as also shown in Table 5. η_{act} reaches values up to 759 mV (at $1.17 \text{ A}\cdot\text{cm}^{-2}$ current density) with $1 \text{ mg}_{cat}\cdot\text{cm}^{-2}$ cathode loading, which represents at least a 93% increase when compared to the values obtained at the same current density with a typical Pt supported on carbon cathode catalyst.³⁴

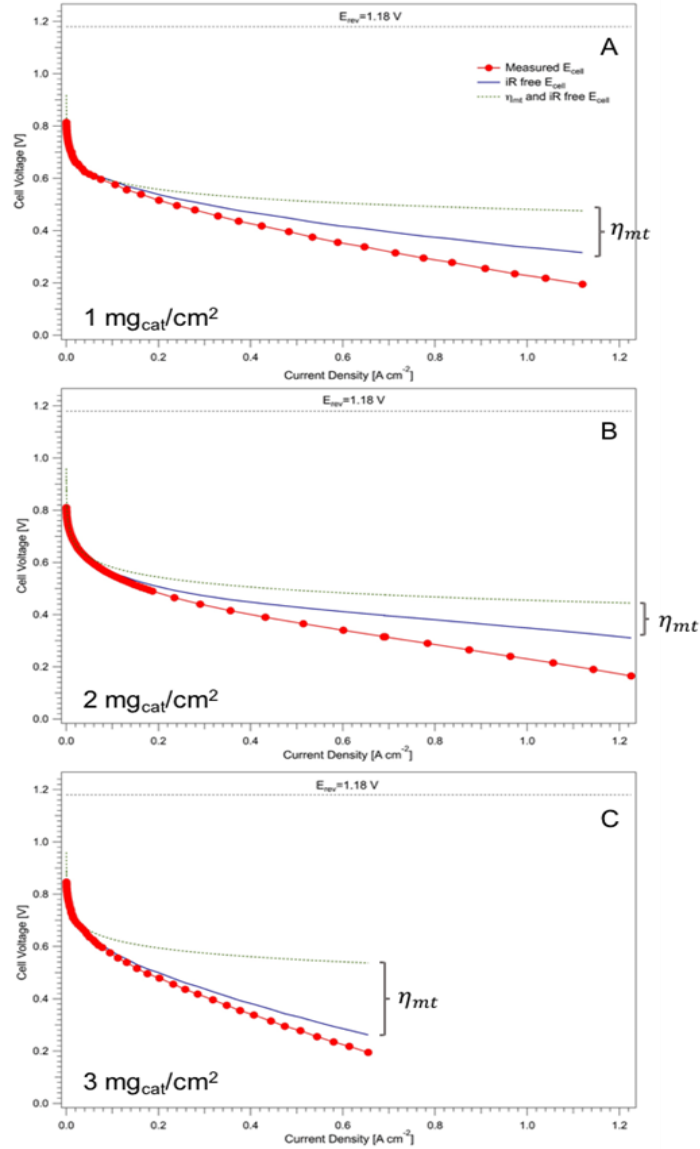


Figure 24. Polarization curve for a PEM fuel cell with 1 $\text{mg}_{\text{cat}}\cdot\text{cm}^{-2}$ (A), 2 $\text{mg}_{\text{cat}}\cdot\text{cm}^{-2}$ (B), and 3 $\text{mg}_{\text{cat}}\cdot\text{cm}^{-2}$ (C) cathode catalyst loadings. Each curve was obtained with inlet gases heated and humidified to 83 °C, 29.4 psia backpressure and the cell temperature was held at 80°C. Calculated polarization curves are also included showing the effect of ohmic and mass transport overpotentials.

Table 5. Ohmic and mass transport voltage loss contributions at a fixed η_{act} and thickness for each cathode loading.

Loading [mg_{cat}·cm⁻²]	Thickness [μm]	η_{act}[mV]	η_{ohm}[mV]	η_{mt} [mV]
1	13.6	630.9	25.92	27.18
		92.2%	3.8%	4.0%
2	46.6	630.4	21.26	33.4
		92.0%	3.1%	4.9%
3	57.3	630.5	27.18	220.5
		71.8%	3.1%	25.1%

In Figure 24, the solid line and the circle symbols represent, respectively, the mass-transport-voltage free cell voltage (result of the addition of the theoretical polarization curve and the measured ohmic losses) and the measured polarization curve. These polarization curves demonstrate the role of the ohmic and mass transport overpotentials on the overall performance of the fuel cell. To quantitatively appreciate this effect, the individual ohmic and mass transport contributions presented in Table 5 were calculated at fixed activation overpotential ($\eta_{act}=632$ mV). From Table 5 it can be observed that the mass transport overpotential becomes more significant for a $3\text{mg}_{cat}\cdot\text{cm}^{-2}$ cathode loading, playing a major role in bringing about the poorer performance obtained in comparison to the lower loadings. The measured thickness values for each loading are presented in Table 5, showing a direct correlation with the cathode catalyst loading.

In summary, through the analysis of the individual contributions to the voltage loss, a combined effect of both kinetic and mass transport contributions can be associated with the cathode loading influence on the cell performance shown in Figure 16. Although the highest cathode loading ($3\text{ mg}_{cat}\cdot\text{cm}^{-2}$) studied implies a higher number of active sites and, therefore, exhibits lower activation overpotential, this effect is counterbalanced by the significantly higher mass transport contribution (Table 5). This increase in the concentration overpotential could be related to larger mass transport limitations due to the thickness of the electrode. This effect might be reduced by increasing the active site density. To assess the

effect of a higher density of active sites in the non-precious material, the performance of an 'ideal electrode' with reduced mass transport losses (η_{mt} obtained at $2 \text{ mg}\cdot\text{cm}^{-2}$) and ORR overpotential (η_{act} obtained at $3 \text{ mg}\cdot\text{cm}^{-2}$) was evaluated. The polarization and power curves for said material are presented in Figure 25, along with those of the best-performing loading ($2 \text{ mg}_{cat}\cdot\text{cm}^{-2}$). As shown in Figure 25, an increase in the density of active sites improves the cell performance throughout the entire voltage range, increasing the maximum MEA power density to $0.65 \text{ W}\cdot\text{cm}^{-2}$ (45% increment with respect to the best performing cathode loading).

Finally, we emphasize some aspects of our test methodology that we believe will be important as more reports of fuel cell tests of these catalysts are done in air, rather than the more common tests in oxygen. Of course, the former is the true practical test of the catalyst in a fuel cell. We suggest that it is important to effect a separation of kinetic and mass transport losses by testing in diluted oxygen streams as a first step in assessing the qualities of a catalyst and the electrode formed from that catalyst. In the absence of an accurate estimate of the number of active sites per unit amount of catalyst, this could allow us to probe indirectly the site density through comparing the onset point for significant mass transport effects, perhaps by analyzing Damköhler numbers.¹³⁴ Also, the inclusion of many more data points in the kinetic region of the polarization curve allows a more detailed kinetic analysis. Furthermore, each of these methods anticipates the

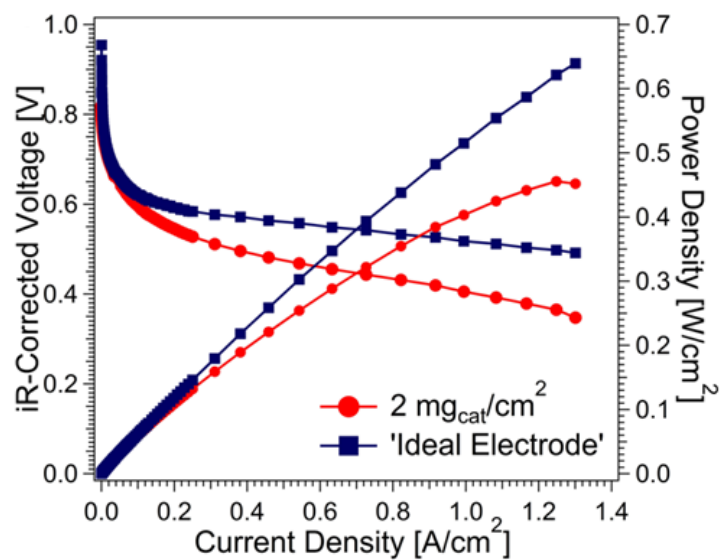


Figure 25. Polarization and power curves for a PEM fuel cell with an ideal cathode result of the combination of the minimum overpotential losses and with $2 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ cathode catalyst loading (best-performing loading).

requirements of modeling by providing more robust data sets that can be fit with greater statistical significance through simultaneous fitting of the family of curves as a function of oxygen partial pressure and through allowing the kinetics to be fit in a less cursory fashion than is typical. Indeed, our approach even lends itself to determining kinetic parameters outside the context of a given modeling framework, allowing a possible reduction in the number of adjustable fitting parameters for analysis of the entire polarization curve.

3.9 Conclusions

A pyrolyzed covalent heme framework was evaluated as a catalyst for the ORR. Pyrolysis followed by acid treatment was shown to be a determinant step towards the catalytic activity of this material. The H_2/O_2 -Ar MEA performance was evaluated for different catalyst loadings and oxygen partial pressures to assess the mass transport influence on the performance of this material.

Through the analysis of the individual contributions to the voltage loss, a significant influence of the transport processes on the overall performance can be observed when the catalyst loading increases. A significant improvement of the overall cell performance was observed when the mass transport losses were ‘artificially’ reduced for the highest cathode catalyst loading.

Chapter 4

STUDY OF THE MICROSTRUCTURE AND PROPERTIES OF A PEMFC CATALYTIC LAYER

Abstract

In this study, a set of experimental techniques is adopted to characterize the fundamental properties of machine-prepared cathode catalyst layers (CCLs) formed by different Pt to C (Pt:C) ratios, a highly graphitized carbon (EA carbon) and 3M ionomer (825EW) with a fixed ionomer to carbon (I:C) ratio. Scanning electron microscopy, transmission electron microscopy and Brunauer-Emmett-Teller nitrogen adsorption were conducted to investigate the CCL microstructure including material dispersion and porosity. This analysis was performed on both the CL in an as-prepared condition and after being subjected to a standard Polymer Electrolyte Membrane Fuel Cell (PEMFC) protocol. The Pt:C ratio had a significant influence on the CCL structure and transport properties. The lowest Pt:C ratio (30:70) exhibited a higher volume of secondary pores and a higher proton conductivity over the whole relative humidity range. Such behavior was associated with a more homogeneous ionomer distribution throughout the CCL and resulted in an enhanced PEMFC performance. A high volume of macropores and high ionomer proton conductivity are correlated with the highest cell performance achieved with the lowest Pt:C ratio tested.

4.1 Introduction

The thin-film composite CL is a central component of PEMFCs. This layer, located at the electrode/membrane interface, comprises the region where the

electrochemical reactions take place. Both the HOR and the ORR require a catalytic material to break the molecular bond of the diatomic gaseous reactant molecules, given the low-temperature conditions in a PEMFC.²

Pt and its alloys have prevailed as the PEMFC catalysts par excellence, due to their high activity towards both HOR and ORR, and its stability under standard operating conditions. However, the high cost and limited availability of the precious Pt metal set a cap on the maximum Pt loading for this technology to be economically feasible. The US DOE have established a $0.125 \text{ g}_{\text{Pt}}\cdot\text{kW}^{-1}$ total loading target at 150 kPa (abs) for a transportation PEMFC stack.³⁵ Such a balance between performance, durability and low Pt loading represents a challenge, especially on the cathode side, where the ORR kinetics tend to be slower.

4.1.1 PEMFC Catalyst Layer Evolution

The CL design has undergone significant changes in the last six decades. First-generation CLs were comprised of Pt black as the electrocatalyst and PTFE as the bonding material.³ FCs equipped with this design, such as the one used in the Gemini missions during the early 1960s, provided high performance with typical Pt loadings of $3.9 \text{ mg}_{\text{Pt}}\cdot\text{cm}^{-2}$ and greater.³ Therefore, the high price of Pt constituted the main limitation for commercialization of this technology.

To reduce cost, diverse approaches were explored in the subsequent decades.^{26,135} An adaptation from phosphoric acid fuel cell electrodes proposed by Raistrick in 1989 represented a major advance.¹³⁶ In this design, the CL consists of carbon-supported Pt particles (~2 nm diameter), sitting on a base layer of carbon black, which is, in turn, spread over a carbon paper or carbon cloth.⁴ This corresponds to the so-called 'ELAT' for electrode-Los Alamos type. PTFE is employed as bonding material, promoting gas diffusion passages due to its hydrophobic nature, which inhibits droplet formation. The active side of the finished electrode is impregnated with a solubilized form of PFSA ionomer (e.g., Nafion®), to guarantee access of the protons to the Pt particles by increasing proton transport within the electrode.¹³⁶ Although these low Pt loading electrodes ($\leq 0.5 \text{ mg}_{\text{Pt}} \cdot \text{cm}^{-2}$) provided similar performance to that achieved with the first-generation CLs, low catalyst utilization (~10-20%) and reproducibility problems motivated the search for alternatives.^{4,137} 20-40% PTFE contents and 0.8-1 I:C ratio were found to be optimal conditions for PEMFC performance when this CL design is employed.²

The widely used 'thin-film' CL system (Figure 26) was initially developed by Wilson and Gottesfeld in 1992.^{4,138} This consists of an ionomer-bonded hydrophilic CL,

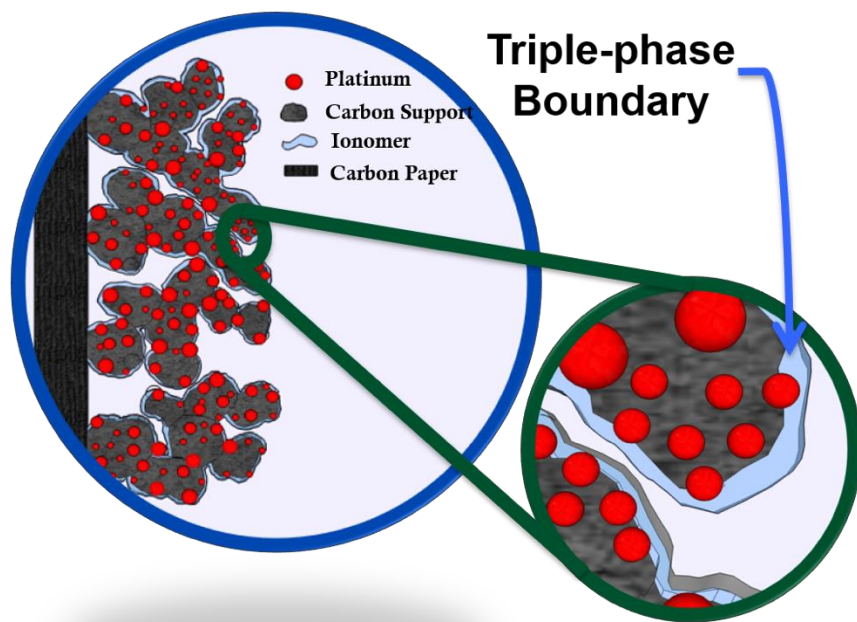


Figure 26. Schematic representation of an ionomer-bonded hydrophilic electrode.

which ensures a larger contact area between the catalyst particles and the ionomer.⁴ For such CLs, Pt utilization has been found to be up to 45.4%, with very low catalyst loadings ($0.12\text{--}0.16\text{ mg}_{\text{Pt}}\cdot\text{cm}^{-2}$) and thickness ($<10\text{ }\mu\text{m}$).¹⁴ As mentioned above, the catalyst utilization depends largely on the contact of gas reactants, protons and electrons. Figure 26 schematically illustrates the three-phase boundary in this CL design, the region where all three components (pore, Pt/C and ionomer) converge and all species have access: electrons travel through the carbon-supported catalyst, protons travel through the ionomer network and the reactant gases travel through void space. It is important to note that this approach does not include a hydrophobic agent within the active layer of the electrode, unlike some previous ones. This is one important novelty of this design, which allowed to achieve higher Pt utilization by eliminating altogether the need for PTFE. This implies, however, that the gases diffusing through the CL must travel through pores in the cathode that are at least partly filled with water in operation. Accumulation of liquid water or “flooding” of the CL can deteriorate the PEMFC performance.^{139,140} Durability of this type of CL largely depends on the stability of the support (i.e. carbon corrosion) and the ionomer. This CL design is the one employed in this work.

Ultrathin catalyst layers, also known as nano-structured thin film (NSTF) CLs, have been considered as a promising alternative to the ‘conventional’ thin film CLs. In this ionomer-free design, the catalyst is typically dispersed on a nanostructured

support, such as gold or carbon.^{27,141} The 3M NSTF electrode, for instance, employs a thin film of platinum-covered crystalline organic whiskers as the catalyst support.^{141–143} The 3M design, which is 20-30 times thinner than 'conventional' CLs, has shown high catalytic activity and durability. NSTF catalysts have shown a five-fold or greater increase in specific activity vs high surface area Pt/C.^{144,145} This gain in catalyst turnover has been associated with the thin-film nature of the NSTF catalyst. However, the significant thinness of the NSTF CL makes it more likely to flood under operating conditions, one of the main technical issues of this design.

Direct dispersion of Pt on the gas diffusion layer or on the electrolyte membrane have also been explored as possible CL fabrication alternatives.^{146–148} Sputter and pulsed laser deposition have been implemented to obtain PEMFC electrodes with low Pt loading ($<0.1 \text{ mg}_{\text{Pt}} \cdot \text{cm}^{-2}$). Despite the remarkable power densities obtained with directly-deposited electrodes, the results are still not comparable to that obtained with 'conventional' CL electrodes.¹⁴⁶

4.1.2 PEMFC Catalyst Layer Components

In general, as illustrated by the previous discussion, the CL is constituted of three components: the electrocatalyst, a high surface area support material and a binder material. The discussion in this section is focused on 'thin-film' CLs.

4.1.2.1 *Electrocatalyst*

Platinum is the most active single metal for the ORR. One of the biggest challenges in PEMFC development is the high Pt loadings required to achieve a good performance. On the anode side, however, sufficient HOR catalytic activity and stability can be guaranteed with low Pt loadings. Combinations of Pt with less noble metals have also been employed to counteract the effect of potential contaminants in the anode feed stream. Most efforts have been focused, therefore, on decreasing the cathode Pt loading without sacrificing PEMFC performance.

The task of decreasing the dependence on Pt has been approached from different perspectives. In another chapter we discuss in detail the efforts to replace the precious catalyst for a PGM-free catalyst. In this section, we will focus on Pt-based electrocatalysts.

Catalytic activity of Pt particles shows a strong dependence on particle size and shape.^{149–151} In principle, particle size is inversely proportional to the surface-area-to-volume ratio, implying a larger accessible active surface area per gram of catalyst. However, this effect is counteracted by a loss in catalytic activity for particle diameters below 4 nm, setting a cap for Pt utilization improvement. Several factors have been associated with this trend. The most representative ones will be discussed in this section

4.1.2.1.1 Crystallographic Orientation

The particle-size dependence can be related to changes in the distribution of platinum facets on the nanoparticle surface.^{151–153} Single-crystal studies have allowed the study of the influence of this factor. For instance, atoms on a Pt(111) surface experience a higher coordination number by other surface and subsurface atoms than atoms on Pt(110) surface. The activity change towards ORR on different Pt facets depends on the energy of adsorption of the O₂ molecule on the surface.¹⁵⁴ Markovic et al. studied the ORR in HClO₄, a non-adsorbing electrolyte, and H₂SO₄ on Pt low index surfaces. In their study, the catalytic activity, discerned from the half-wave potential, decreased in the sequence Pt(110)>Pt(111)>Pt(100) in HClO₄ and Pt(110)>Pt(100)>Pt(111) in H₂SO₄.¹⁵⁴ Bisulfate anion adsorption inhibited ORR catalytic activity in the presence of sulfuric acid as an electrolyte.

Furthermore, a study by Kinoshita suggested a correlation between the fraction of surface atoms on the Pt(1 0 0) and (1 1 1) facets and the mass activity and specific activity of the Pt cubo-octahedral structures.¹⁵⁵ This trend, which was observed with H₂SO₄ electrolyte, was attributed to stronger adsorption of oxygenated species (i.e. sulphate anions) on the smaller (lower surface atoms fraction) particles, which would hinder the ORR. However, this approach fails to explain the same particle size trend in non-adsorbing electrolytes such as HClO₄.^{149,156,157} Therefore, other variables are significant in explaining the catalyst activity trends.

4.1.2.1.2 Pt electronic state

Takasu et al. have provided a different explanation for the particle size effect.¹⁵⁷ Based on XPS results, the particle size dependency has been attributed to the stronger interaction of oxygen with smaller Pt particles due to changes in the electronic state of Pt. XPS results showed a shift of the binding energy of Pt4f_{3/2} and Pt4f_{5/2} towards a higher value when the particle size decreased.

This hypothesis, however, has been debated, ascribing the 'apparent' increase in binding energy to an artifact of the technique.^{158,159} However, in-situ XAS studies led to a similar conclusion.¹⁵⁶ Strong adsorption of OH, which can inhibit the ORR, was observed for particle sizes below 50 Å.

4.1.2.1.3 Pt Surface Defects

In heterogeneous catalysts, metal surface defects are typically more active because the surface atoms in these sites are not fully coordinated and can interact more easily with the substrate molecules. Evidence of this effect on the ORR has been presented by Maciá et al.¹⁶⁰ They studied the ORR on Pt single crystal belonging to the [0 1 $\bar{1}$] zone to explore the effect of the steps and the symmetry of the terrace. In H₂SO₄, Pt(111) terraces were found to be more active than the corresponding facets, which was attributed to the inhibition of the ORR by the formation of a stable bidimensionally ordered adlayer of bisulfate anions. Further exploration by Kuzume et al. showed that two effects contribute to the ORR

structure sensitivity: anion adsorption and oxide formation on the electrode surface.¹⁶¹

4.1.2.1.4 The Potential of Zero charge (pzc)

The pzc, defined as the point at which the free, electronic excess charge density plus the charge density transferred during adsorption equals zero, has also been explored as a determining factor for the ORR catalyst activity.¹⁶² Mayrhofer et al. found a ~35mV pzc negative shift when particle size decreased from 30 nm to 1 nm in a HClO₄ solution.¹⁶³ This pzc reduction can lead to an enhancement of the energy of adsorption of anions and the associated blockage of the ORR active sites.

4.1.2.2 *Support*

Carbon black and graphitized carbon are typically used as support materials in the PEMFC electrodes. These low cost, and chemically stable materials exhibit surface areas ranging from <10 to >2000 m²·g⁻¹.^{164,165} With a tendency to aggregate, carbon black exhibits a bimodal pore size distribution: 2-20 nm sized pores laying within carbon particles agglomerates (known as primary pores) and >20 nm sized pores between aggregates of agglomerates (known as secondary pores).

The CL structure has been found to be strongly dependent on the native carbon support.^{5,166} KJB-based CLs, for instance, exhibited higher pore volume than

Vulcan-based CLs at the same ionomer loadings. Particularly, KJB-based CLs retained higher primary pore volumes. This observation suggests that ionomer distribution occurs mainly on the surface of carbon agglomerates, with the associated coverage of the secondary pores as has been proposed by Eikerling et al.¹⁶⁷ This effect was observed with ionomer loadings as low as 5 wt. %. On the other hand, Park et al. found that a large portion of Pt nanoparticles penetrate into the KJB carbon nanopores, which can lead to lower ORR performance.¹⁶⁸

Durability is, however, the biggest challenge with the use of carbon supports. Surface oxidation and carbon dioxide evolution can lead to carbon corrosion during PEMFC operation.¹⁶⁹ This degradation of the support is detrimental to the catalyst activity as it causes catalyst particle detachment, migration and subsequent coalescence.

4.1.2.3 Ionomer

The effect of different levels of ionomer loading, particularly using Nafion, has been widely investigated in thin-film CLs.^{170–173} Studies have shown limitations in the CL proton conductivity (σ_{CL,H^+}) at low ionomer contents, which have been associated with the difficulty to form a continuous ionomer network.¹⁷³ On the other hand, an excess of ionomer can obstruct gas access to the reactive sites, hindering the reaction progress. Optimum Nafion loading in the CL has been reported to lie within the 30-40 wt.% range.^{173,174} However, this value significantly depends on

the carbon support structure.¹⁷⁵ Furthermore, the nanostructure of the ionomer can also be critical for the wide range of transport processes taking place in the CL.

Although the PFSA ionomer membrane structure has been extensively studied,¹⁷⁶ the properties of a confined thin-film ionomer are still not well understood. Several studies have shown that Nafion exhibits a heterogeneous distribution inside the CL with a 2-10nm thickness.¹⁶⁵ Such confinement can drastically affect the ionomer structure orientation and, therefore, the mechanisms of proton conduction and overall CL performance. Proton conductivity studies involving recast polymer films on a flat substrate have indicated intrinsic differences when compared to the bulk material.^{177,178}

In the CL, the specific nanostructure is determined by the relative strength of interaction of the ionomer with the carbon, Pt or with itself; these are in turn related to the structure of the ionomer and its degree of functionalization with sulfonic acid groups. Indeed, some indications of specific adsorption of sulfonate groups on specific crystal faces of Pt have been reported.^{179,180} This observation has led to widespread speculation that the sulfonate group interacts strongly with Pt particles in the CL, thereby 'poisoning' the Pt for ORR. Electrode performance is affected by several key properties of the ionomer component, such as conductivity and water uptake, which in turn are affected in various ways by the ionomer distribution.

4.1.3 CL Properties

4.1.3.1 Ionic Conductivity

High ionic conductivity in the CL is necessary to achieve high fuel cell performance. Protons need to successfully reach the active sites in the CL for the reaction to take place. Therefore, a 'proton transfer resistance in the CL' term has to be considered in the high-frequency fuel cell resistance.

Proton transport in the CL is closely linked to water uptake and therefore, depends on morphological changes.¹⁸¹ Two mechanisms have been associated with proton conduction (Figure 27): structural (Grotthus mechanism, also known as proton 'hopping')¹⁸² and vehicular diffusion. The former was described by Agmon as a series of hydrogen-bond-breaking and forming steps, resulting in a net proton transfer.¹⁸² This so-called 'hopping' benefits from fully hydrated conditions, where the fast (~1.5 ps) rotation and reorientation of water molecules can occur. The vehicular mechanism, on the other hand, is the dominant process at low and intermediate hydration conditions and results in slower conduction. Proton conductivity, therefore, is sensitive to water content and, furthermore, to the ionomer morphology. To illustrate the relation between water and ion transport, a comparison between water's self-diffusion (D_{μ}) and ionic diffusion (D_{κ}). The Nernst-Einstein equation (Equation [25]) is typically used to describe the ionic diffusion.^{165,181}

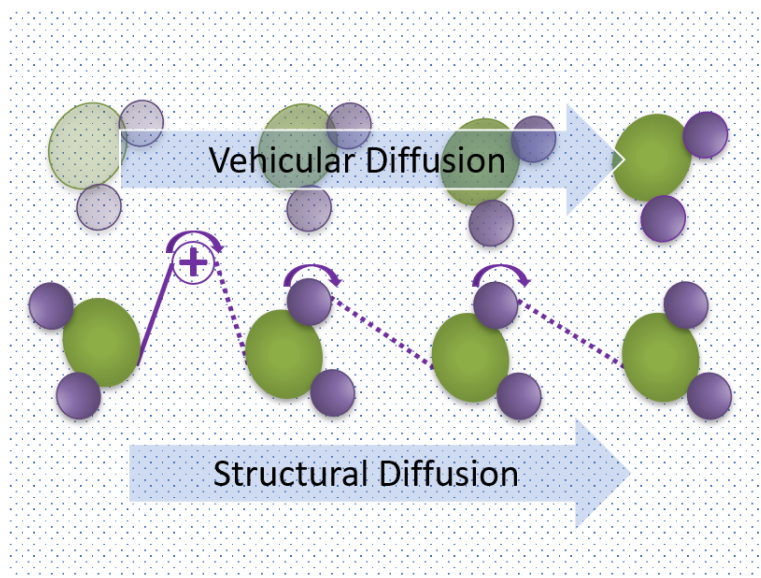


Figure 27. Illustration of proton-transport mechanisms: vehicular (top) and structural (bottom) diffusion.

$$D_{\kappa} = \sigma \frac{RT}{F^2} \frac{1}{c_{H^+}} \quad [25]$$

Where F is Faraday's constant, c_{H^+} the proton concentration, T is the temperature, R is the gas constant and σ is the proton conductivity. Calculations of the water diffusion coefficient from NMR and of the ionic diffusion coefficient via measurement of the proton conductivity have been reported previously.^{183,184} Although $D_{\kappa} \cong D_{\mu}$ at low water uptake (λ), $D_{\kappa} > D_{\mu}$ with increasing λ . This trend has been attributed to the different mechanisms taking place at the low and high-water-uptake regimes (Figure 27), as discussed above.

From the previous discussion it follows that ionomer distribution throughout the CL can be a determining factor for the proton conductivity and, ultimately, for the PEMFC performance. A more continuous ionomer pathway in the CL is required for the electrochemical reaction to take place. Several studies have shown that the proton conductivity decreases in ionomer thin films and in PEMFC catalyst layers relative to that in bulk membrane materials. Factors such as the carbon pore network, the ionomer content and the catalyst particle size can influence ionomer distribution and, therefore, affect the proton and water transport mechanisms. Recent work by Weber's group suggests that confinement of the ionomer as an adsorbed thin film decreases water uptake and conductivity. This suggests that interactions with the support can also directly reduce conductivity.

Determining the ionic conductivity requires separating electronic and ionic contributions in the mixed conductor that is the composite CL. *Ex situ* measurements were first reported by Saab et al. using combinations of ionic and electronically conductive contacts to separate the two contributions.¹⁸⁵ Several studies investigating conductivity *in situ* have used a simplified transmission line model for its measurement.^{31,186} This model treats the potential loss associated with the HOR as negligible, under the assumption that this reaction is fast enough that the proton transfers through a very short pathway. Operating on a H₂/N₂ system also eliminates the charge transfer resistance of the ORR. EIS measurements are carried out at a sufficiently high potential to ensure that the cell is running at the limiting current and, therefore, that the AC impedance signal is not influenced by the hydrogen crossover. High potentials also ensure that the CL capacitance is independent of the RH. The transmission line model corresponding to such conditions is shown in Figure 28, reproduced from the study of Liu et al.¹⁸⁶

4.1.3.2 *Water uptake*

Water adsorption and transport in Nafion thin-films have been examined by several studies.^{187–190} Sun et al. studied water uptake and transport of water within homemade CL films.¹⁸⁸ Using a combination of NMR probes reporting on local (relaxation) and long range (PGSE Diffusion), they concluded that in the low water content regime the local environment for water hydrating the sulfonate groups is

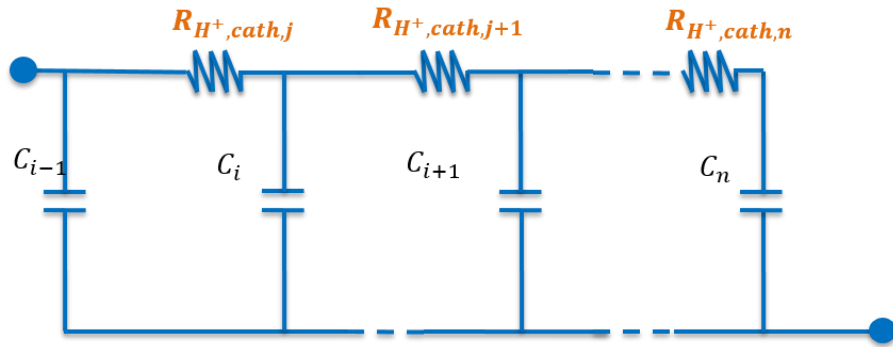


Figure 28. Simplified transmission line model for PEMFC electrodes under H_2/N_2 (Reproduced from Liu et al.)¹⁸⁶

essentially the same in the CL while longer range diffusion is strongly dependent on water content and decreases dramatically as water content decreases. The latter decrease is much stronger than in a membrane. This observation, taken together with the likelihood that all water at low water contents is associated with sulfonates, suggests that decreasing hydration breaks up the connectivity of the ionomer network in the CL.

Unlike the bulk ionomer membrane, the ionomer in the CL also must be permeable to gases. Reactants must be able to diffuse through the thin-film ionomer layer to be able to reach the catalytic reaction sites. Therefore, gas permeability through ionomer thin-films has been an important research focus. Permeability is the product of solubility and diffusion of the gas, oxygen, through the ionomer.²⁷ PFSA ionomers exhibit higher permeability than hydrocarbon ionomers.¹⁹¹

4.1.4 Summary

As illustrated above, there is an interplay between the CL structure and the transport properties in a CL. A vast majority of work has been focused on understanding Nafion's morphology and interaction. However, the emergence of PFSA ionomers with different chemical structure and EW have gained interest in the last years, evidencing the effect that the ionomer structure has on the transport phenomena occurring in PEMFC cathodes.

In this work, we seek to further understand the ionomer distribution and its effect on PEMFC performance. Machine-prepared, free-standing CLs with different Pt:C ratios are analyzed with this purpose. These CLs are composed of a highly graphitized carbon (Tanaka EA-type carbon) and 3M ionomer (825EW) with a fixed I:C ratio. Analysis was performed on the CL in a pristine (before testing) condition and after being subjected to a standard PEMFC protocol. SEM, TEM and BET nitrogen adsorption were conducted to investigate the CL microstructure including material dispersion and porosity. The water uptake and conductivity were determined for each Pt:C ratio as functions of RH. Finally, the free-standing CLs are introduced into fuel cell single cells and tested under various conditions.

4.2 Physicochemical Characterization

Free-standing machine prepared CLs with different Pt:C ratios were provided by 3M for this study. The electrodes provided were composed of Pt-supported Tanaka EA-type carbon, and 3M ionomer (825EW). The EA-type carbon is a graphitized KJB EC600JD carbon. The unmodified KJB EC600JD is a high-surface area ($\sim 1400 \text{ m}^2 \cdot \text{g}^{-1}$ BET area) carbon black material. In general, carbon black materials exhibit a bimodal pore size distribution, which includes the so-called primary pores (2-20 nm diameter) located within agglomerates of carbon particles and secondary pores (>20 nm diameter) between aggregates of agglomerated KJB.^{5,27,30,165} KJB carbon, in particular, also exhibits a significant fraction of micropores (<2 nm)

compared to other widely used carbon black materials such as Vulcan XC-72.⁵ Although KJB carbon is nominally non-graphitized, primary KJB carbon particles display a graphitic structure at/near the outer surface.^{175,192} Further graphitization, usually achieved by applying high current densities or temperatures (>2500 °C), have a positive effect on the resistance of the material to electrochemical corrosion and, therefore, its durability.^{193,194}

Three sets of free-standing CLs were provided as 15x30cm² thin-electrode sheets loosely supported on a paper liner for easy detachment. The general properties of these samples are shown in Table 6, all sets were prepared with a 0.25mg_{Pt}·g⁻¹ loading, 1.0 I:C ratio and 30:70, 50:50 and 70:30 w/w Pt:C ratios. A more uniform and homogeneous electrode area can be guaranteed through this fabrication technique in comparison with hand-made CLs. Free-standing CLs was used instead of a catalyst coated membrane (CCM), to allow the ready application of certain experimental methods.

4.2.1 Microscopy Characterization

TEM images are shown in Figure 29 for the 50:50 Pt:C ratio catalyst powder (Figure 29A) and the set of CLs with 30:70 (Figure 29B), 50:50 (Figure 29C) and 70:30 (Figure 29D) Pt:C ratio prepared through the scraping technique. The characteristic planes and facets of a graphitic carbon can be observed in all cases (green arrows in Figure 29). Preferential Pt deposition in the carbon structure

Table 6. Machine-prepared free-standing electrodes properties.

Sample	Pt:C ratio	Loading [mg_{Pt}·cm⁻²]	Ionomer Type	I:C ratio	Ionomer wt. %
Pt30C70	30:70	~0.25	3M 825 EW	1.00	41.18
Pt50C50	50:50				33.33
Pt70C30	70:30				23.08

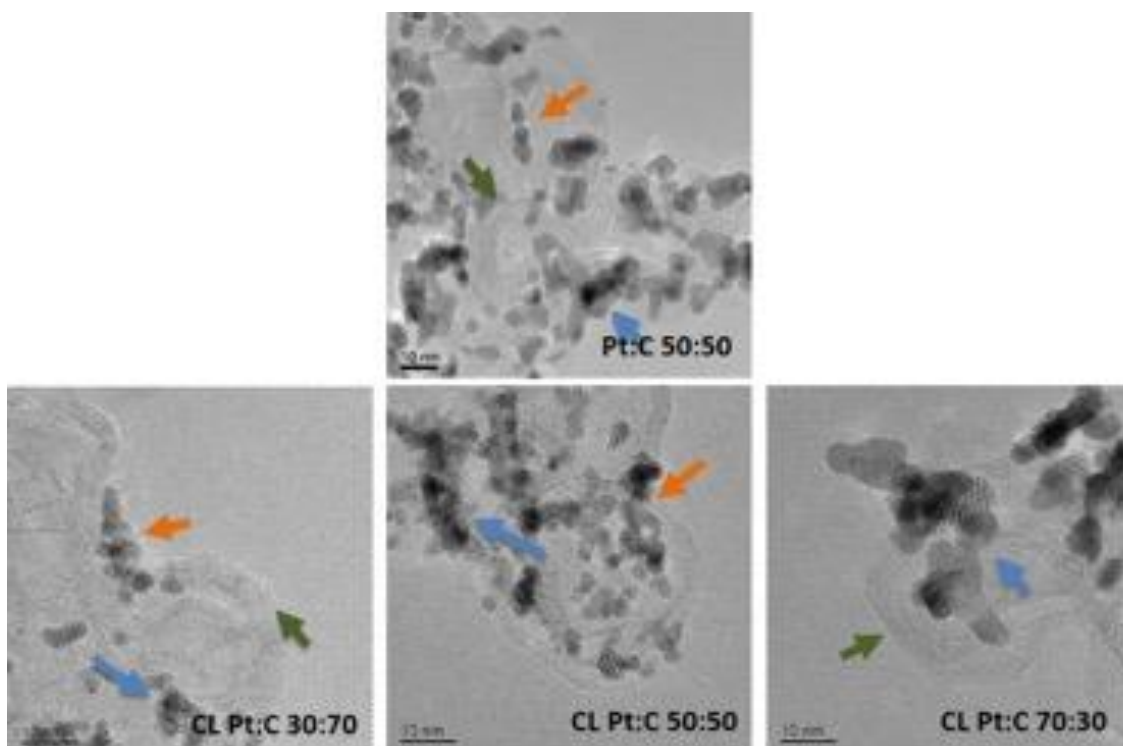


Figure 29. High-resolution (HR)TEM images of 50:50 Pt:C catalyst powder (A), and the scraped 30:70(B), 50:50(C) and 70:30(D) Pt:C machine-prepared free-standing electrodes showing the Pt particles accumulation around the graphitic planes of the carbon support.

defects (orange arrows in Figure 29) lead to a heterogeneous Pt particle distribution throughout the carbon structure and to larger Pt particle agglomeration (blue arrows in Figure 29). The agglomeration effect becomes more significant as the Pt:C ratio increases.

In order to obtain CL cross-sectional specimens, the “full-embedding” ultramicrotomy technique was employed for both fresh and post-operation samples.^{16,17} To obtain the “fresh” samples, small sections of the freestanding electrodes were hot pressed to a Nafion 212 membrane section to guarantee similar conditions to that of the post- operation cathode. These sections were embedded in an epoxy resin and then sectioned with a diamond knife on an ultramicrotome, as described previously.

Figure 30 shows representative images of the 30:70, 50:50 and 70:30 Pt:C fresh electrode samples. It is useful to keep in mind what is *not* detectable in these images. The carbon structure is not as defined in these images as it was in Figure 29, given the epoxy coverage throughout the sample. The presence of the epoxy also prevents the identification of the ionomer phase in these samples. Thus, several key aspects of the puzzle that is the CL, such as the internal structure of the carbon particles and the disposition of ionomer, are not readily visible. The 70:30 Pt:C sample has larger Pt particle sizes and a larger proportion of uncovered

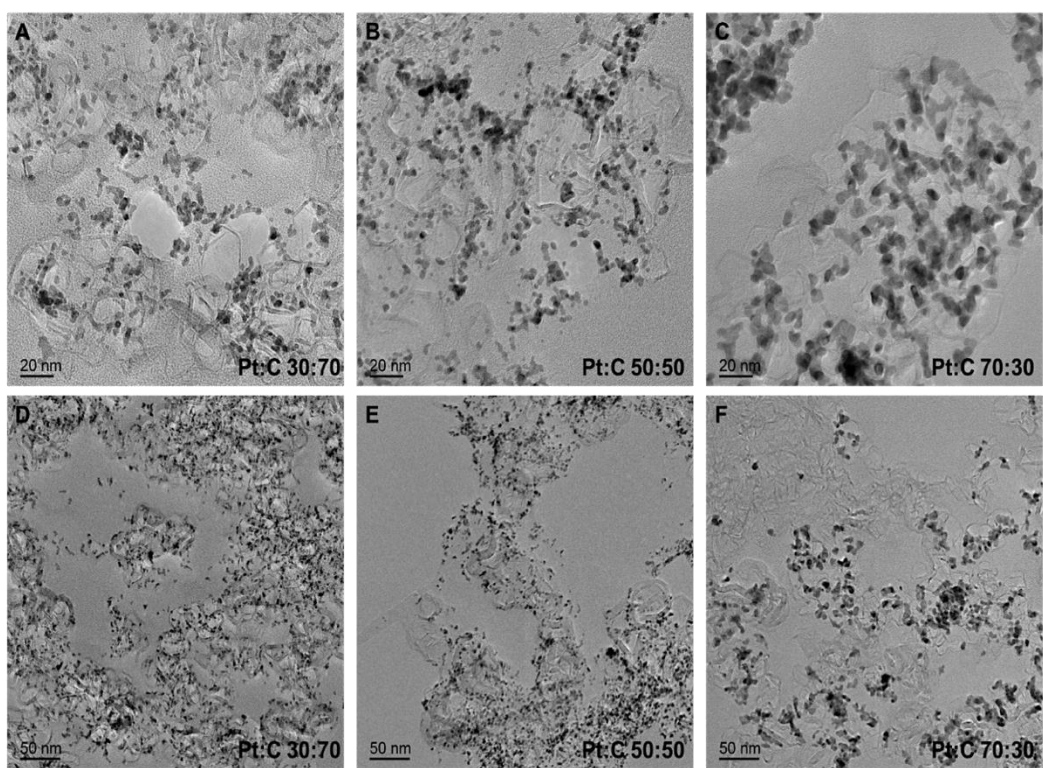


Figure 30. HRTEM images of the epoxy-embedded fresh 30:70 (A,D), 50:50 (B,E) and 70:30 (C,F) Pt:C electrodes. The latter exhibits a higher proportion of Pt uncovered carbon area as a result of a larger Pt particles agglomeration.

carbon areas, as observed in Figure 30 C and F, in comparison to the samples with lower Pt ratio. Significant Pt particle agglomeration is observed with both the higher Pt ratio (50:50 and 70:30 Pt:C) samples.

4.2.2 Pt Size Distribution

Histograms of particles sizes from samples with different Pt:C ratios are shown in Figure 31 and a summary of the statistics is presented in Table 7. All the fresh samples display a significant deviation from the normal distribution, exhibiting a positive skewness outside the range expected from a normal distribution. This asymmetric behavior, however, is expected due to the minimum value restriction (zero diameter) associated with this variable and indicates a higher ratio of small particles.

Among the fresh samples, only the 70:30 Pt:C ratio sample exhibits a kurtosis value within the range expected from a normal distribution.¹⁹⁵ The particle size data for this sample also falls over a wider range (6.554) when compared to the lower Pt:C ratios. Both the 30:70 and 50:50 Pt:C ratio samples exhibited positive kurtosis values, typical of a distribution more peaked in the center. These results indicate a higher heterogeneity in Pt particle size for the sample with the highest Pt:C ratio, reflecting the higher degree of agglomeration observed in Figure 30.

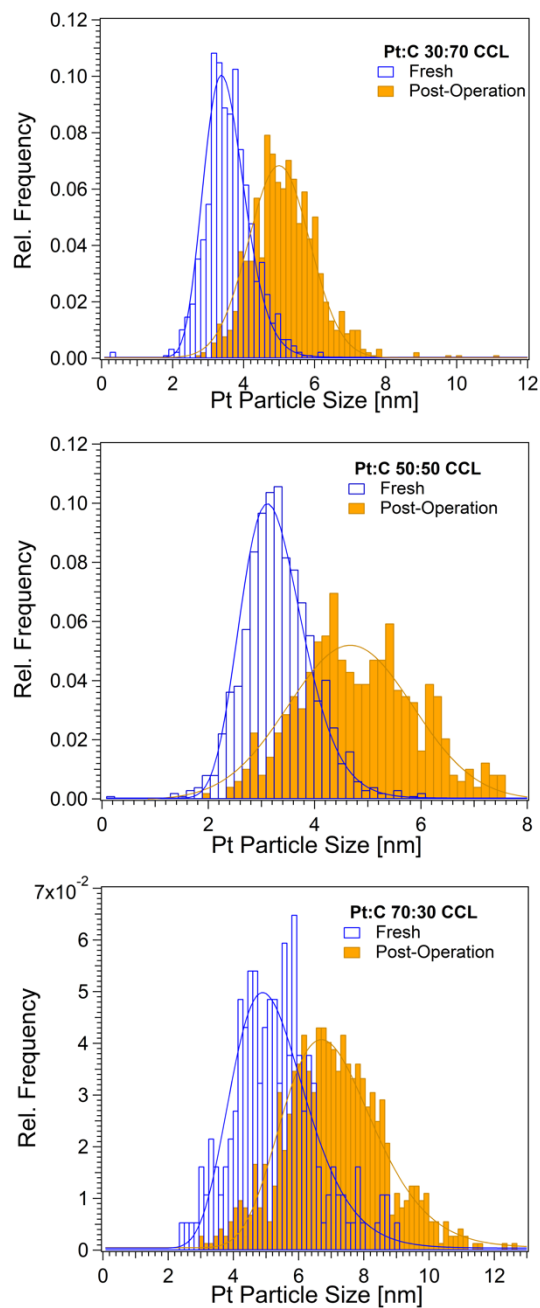


Figure 31. Pt particle size histograms for 30:70, 50:50 and 70:30 Pt:C ratio CLs calculated from the TEM micrograph processing.

Table 7. Summary Statistics for Pt Size Distribution for the fresh 30:70, 50:50 and 70:30 Pt:C ratio CLs.

Pt:C ratio	30:70		50:50		70:30	
Status	Fresh	Post	Fresh	Post	Fresh	Post
Average	3.516	5.075	3.247	4.742	5.206	6.980
Median	3.469	5.008	3.212	4.670	5.160	6.919
Std. Dev.	0.667	0.944	0.6568	1.100	1.300	1.557
Minimum	0.2312	2.576	0.129	1.891	2.309	2.890
Maximum	6.130	11.047	5.943	7.490	8.862	12.493
Range	5.899	8.471	5.814	5.600	6.554	9.602
Std. Skewness	2.544	10.099	3.803	1.481	2.330	2.260
Std. Kurtosis	9.988	18.331	7.738	-1.917	0.672	1.023

Given that none of the fresh observations can be identified as normal distributions of particle size, a robust statistical method is necessary to enable comparison of these samples. In this case, the Kruskal-Wallis (KW) test was found to be suitable, given the non-normality of the data and the existence of outliers in all samples.¹⁹⁶ The KW test tests the null hypothesis that the medians within the 3 fresh samples are the same. This technique established a statistically significant difference between the medians of the Pt particle size for the fresh 30:70, 50:50 and 70:30 Pt:C ratio samples at the 95.0% confidence level. To determine which medians are significantly different, the median notches from the different samples were compared in a Box-and-Whisker plot (Figure 32). Each median notch covers the interval:

$$\tilde{x}_j \pm \frac{z_{\alpha/2}}{2} \frac{1.25(IQR_j)}{1.35\sqrt{n_j}} \left(1 + \frac{1}{\sqrt{2}}\right) \quad [26]$$

Where $\tilde{x}_j$ is the median of the j^{th} sample, IQR_j is the sample interquartile range, n_j is the sample size, and $z_{\alpha/2}$ is the upper critical value of a standard normal distribution. In this case, given that the median notches do not overlap for any of the samples, we can conclude that there is a statistically significant difference amongst the medians of the fresh 30:70, 50:50 and 70:30 Pt:C ratio sample at the 95% confidence level.

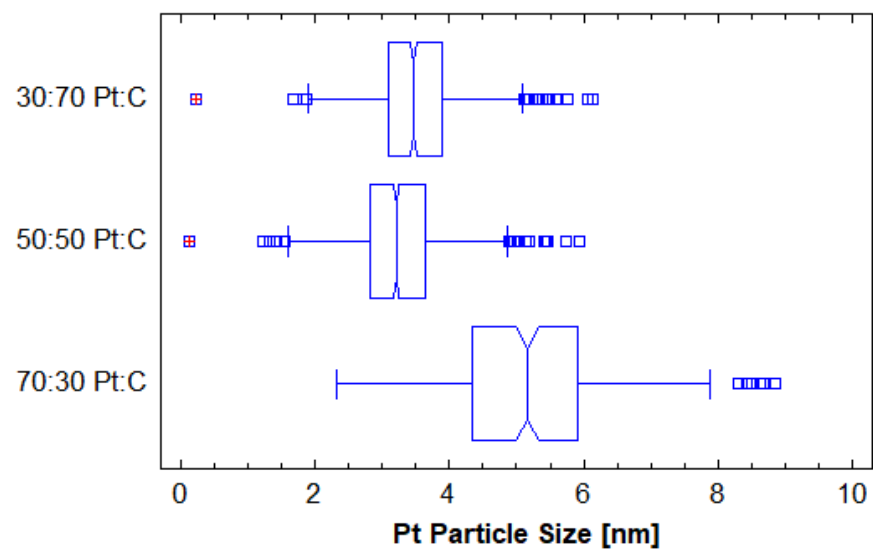


Figure 32. Box-and-Whisker plot of Pt particle size for the fresh samples with 30:70, 50:50 and 70:30 Pt:C ratios.

The calculated average Pt particle sizes are 3.516, 3.247 and 5.206 nm for the 30:70, 50:50 and 70:30 Pt:C fresh samples respectively. The average Pt particle size is significantly higher for the highest Pt:C ratio, which is consistent with the larger agglomeration that is qualitatively observed in the TEM images. The 50:50 Pt:C ratio exhibited the lowest average Pt particle size. This trend was also confirmed through XRD (Figure 33). Particle diameters calculated from the Pt (111) peak exhibited the same trend observed from the TEM calculations ($d_{70:30 \text{ Pt:C}}:10.9 \text{ nm} > d_{30:70 \text{ Pt:C}}:5.8 \text{ nm} > d_{50:50 \text{ Pt:C}}:4.9 \text{ nm}$). Such a difference in average Pt particle size represents approximately a 40% loss of surface/volume ratio when comparing the 70:30 to the 50:50 Pt:C ratio samples. The Scherrer equation ([4]), however, provides a volume-weighted average size, while the TEM analysis performed provides an arithmetic mean size, which explains the higher values obtained through the former.

Several TEM images of the samples subjected to fuel cell standard operation conditions were used to characterize the changes in the Pt size distributions. Figure 34 shows representative TEM images of the 50:50 Pt:C sample before (Figure 34A) and after (Figure 34B) FC operation. An evident increase of Pt size during FC operation can be observed in these images. Pt size distributions for fresh and post-FC operation 30:70 (Figure 31A), 50:50 (Figure 31B) and 70:30 (Figure 31C) Pt:C cathodes are also shown, exhibiting a significant widening and

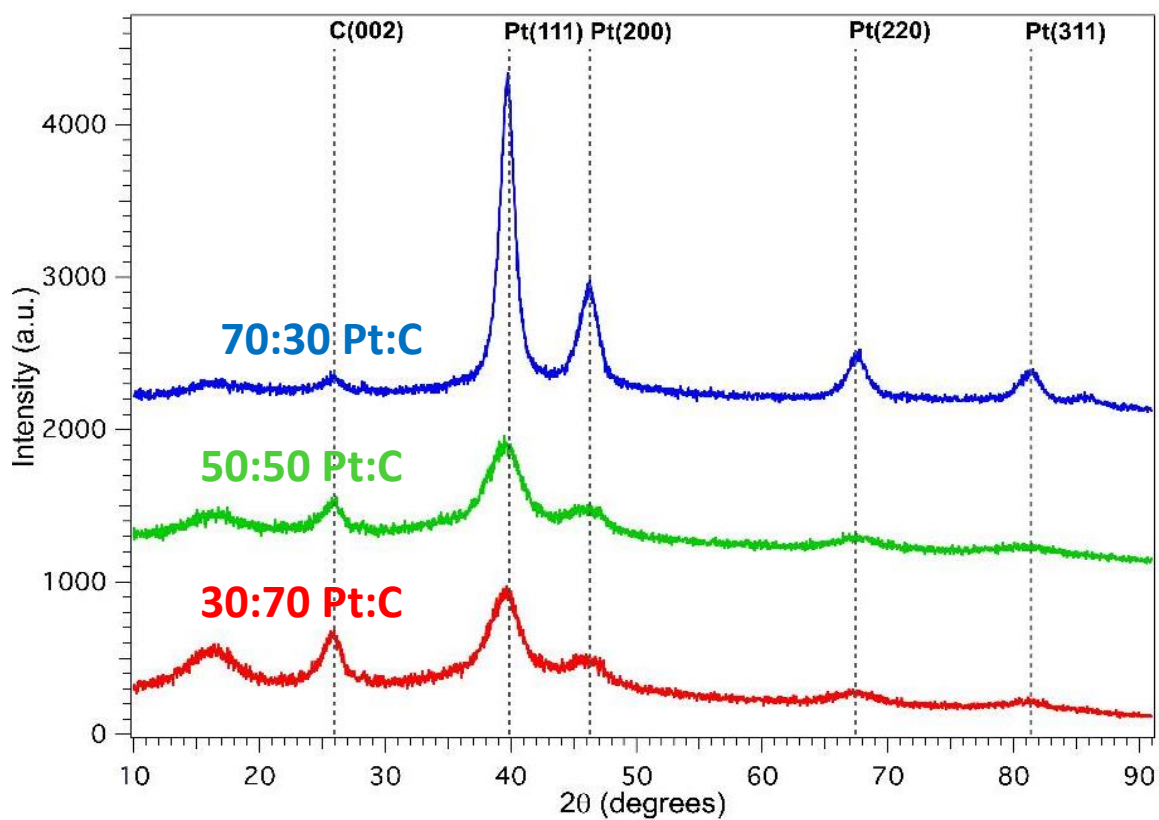


Figure 33. Cu K α XRD patterns for the 30:70, 50:50 and 70:30 Pt:C ratio CLs.

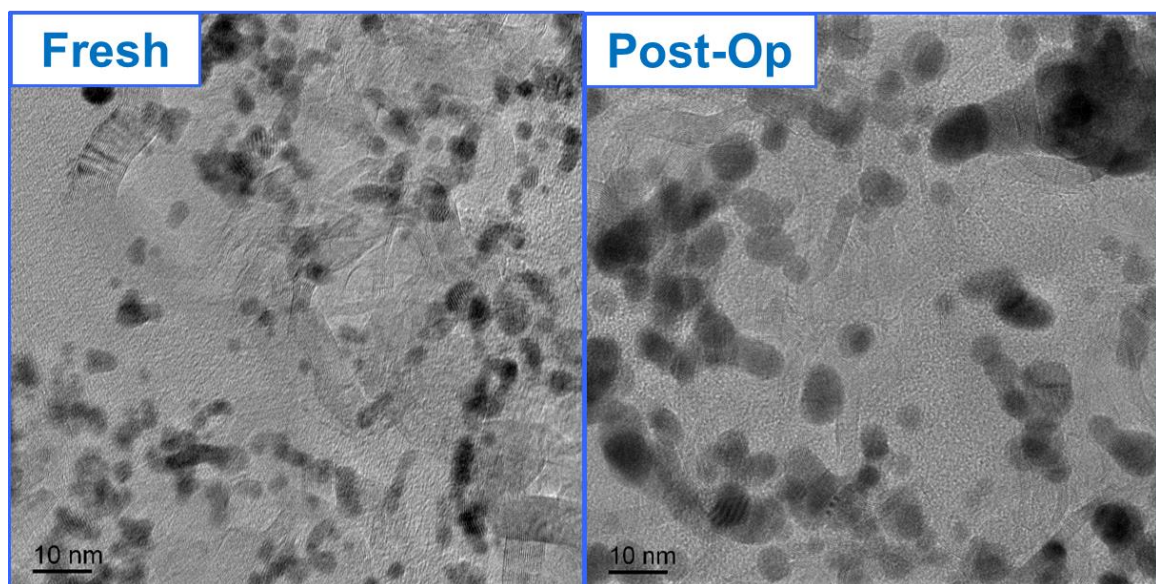


Figure 34. TEM images comparing fresh cathode Pt particles(left) with post-operation cathode Pt particles (right) evincing a Pt size increase during FC operation.

a tendency towards higher Pt particle sizes. This behavior has been associated with the combination of two processes during FC operation: crystallite migration and coalescence, and Ostwald ripening.^{16,197} The former process promotes total surface energy minimization without involving particle dissolution, and is characterized by a Pt size distribution with peaks at small sizes, tailing toward larger sizes. The electrochemical Ostwald ripening effect involves the dissolution of smaller particles and its further redeposition on the larger particles surface, and it features an asymmetric particle size distribution with a tail toward a small particle end due to the smaller particles dissolution.¹⁹⁷

Among all the samples, only the post-operation 50:50 Pt:C ratio sample produced skewness and kurtosis parameters within the range expected for a normal distribution. Given the non-normal distributions of the other samples, the KW test was also employed to compare the post-operation samples. A statistically significant difference was also established in this case at a 95% confidence level, and a similar trend to the one observed with the fresh samples was maintained.

4.2.3 Pore Size Distribution

The N₂ adsorption/desorption isotherms for the catalyst powder and the set of CLs are shown in Figure 35. In general, all samples exhibit a similar hysteresis behavior. Hysteresis has been associated with the cavitation mechanism of condensed nitrogen in the pores, which shifts the desorption plot to lower relative

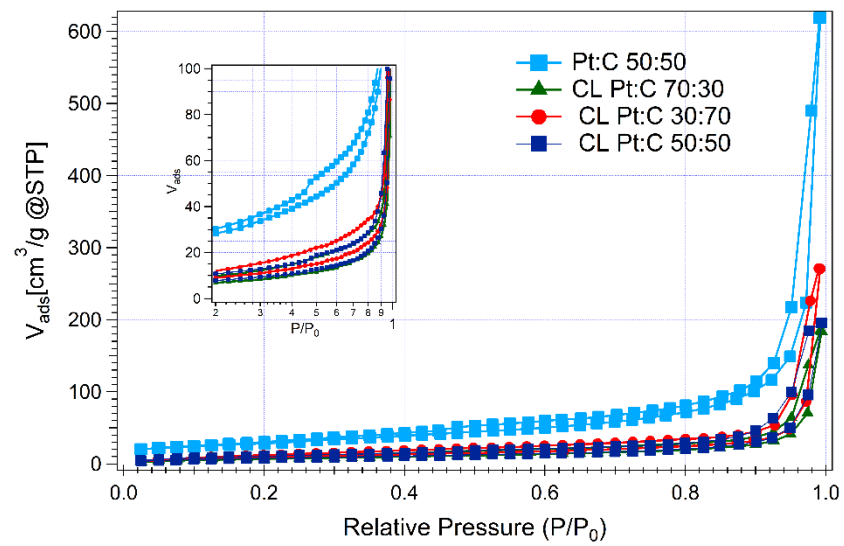


Figure 35. N₂ adsorption/desorption isotherms for the 50:50 catalyst powder, and the 30:70, 50:50 and 70:30 Pt:C ratio CLs.

pressures.¹⁶⁸ This suggests the presence of a porous structure on the carbon support that is maintained in the CL despite ionomer presence.

The pore size distributions shown in Figure 36A were calculated from the N₂ adsorption/desorption measurements using the BJH method.²⁴ The pore structure shows qualitatively similar features in all cases, exhibiting two characteristic peaks: wide in the secondary (>20 nm pore diameter) pore region and sharp in the primary (3-20 nm pore diameter) pore region. An evident pore volume decrease occurs for all CL samples when compared to the catalyst powder, because of the ionomer penetration into the pores, which has been assumed to occur mainly in the surface of carbon agglomerates (>20 nm diameter mesopores).^{5,30,31}

Among the CL samples, the 70:30 Pt:C ratio presents a slightly higher primary pore (small pores) volume, and the 30:70 Pt:C ratio sample exhibits the highest secondary pore (large pores) volume as can be observed in Figure 36B, where the cumulative pore volume over the 3-20 nm and 20-220 nm ranges are presented for both the 50:50 Pt:C powder and the CL samples. Given that both the carbon support and the I:C ratio are fixed for the CL samples in this study, we can affirm that the Pt:C ratio has a significant influence on the ionomer distribution throughout the CL and, therefore, on the resultant CL pore network structure. A theoretical model developed by Ishikawa et al. showed that ionomer coverage on Pt surface decreases with an increase in the Pt:C ratio.¹⁹⁸ This behavior can be potentially caused by a higher affinity of the ionomer towards the carbon surface, which has

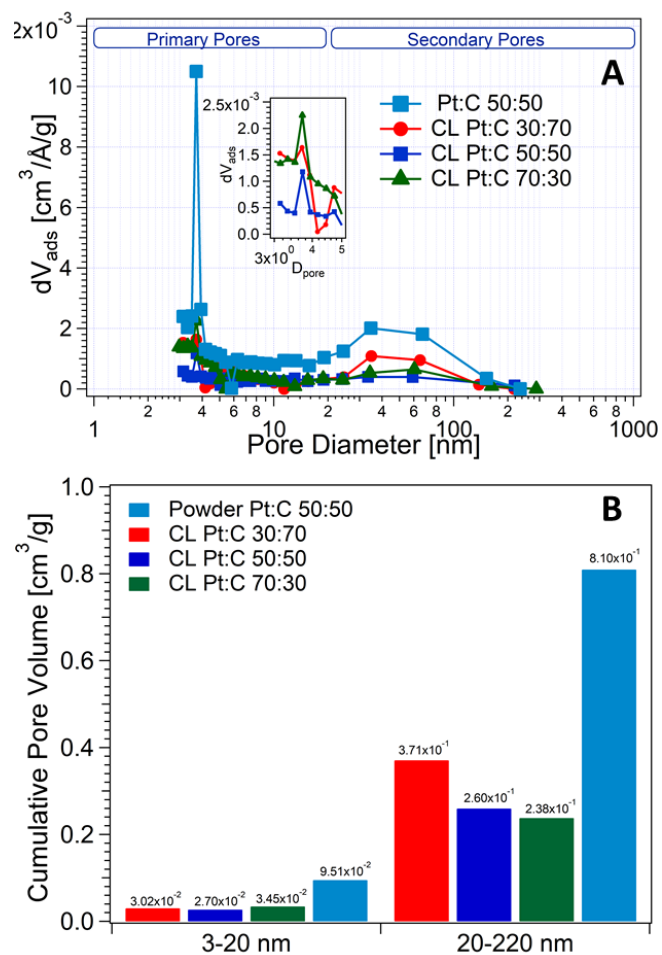
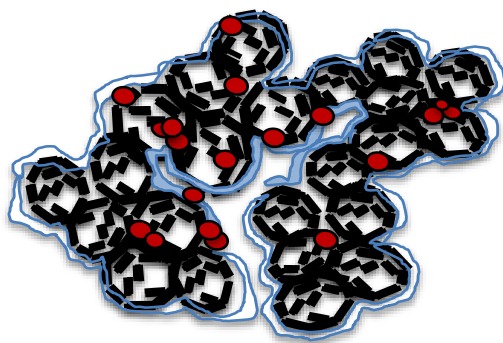


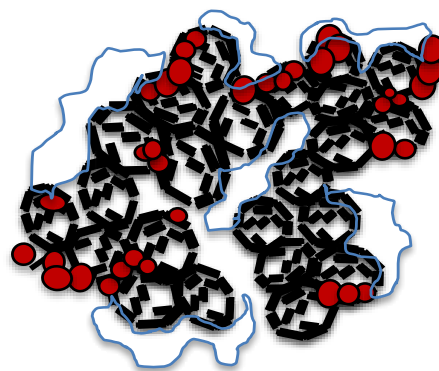
Figure 36. PSD (A) and cumulative pore volume (B) for the 50:50 catalyst powder, and the 30:70, 50:50 and 70:30 Pt:C ratio CLs showing a bimodal pore size distribution in all cases.

been suggested by previous PFSA ionomer adsorption studies carried.^{199,200} This effect, along with the significant Pt particle agglomeration observed in the 70:30 Pt:C CL sample through TEM characterization (Figure 30) can lead to higher ionomer agglomeration on the >20 nm mesopores, thus reducing the 'available' pore volume in this size range.

In Figure 37, schematics of the Pt:C ratio effect on the Pt and ionomer distributions at a graphitic carbon support are shown summarizing the information obtained from the TEM and BET studies. On this type of carbon, Pt particles typically exhibit a tendency to accumulate in the structure defects and edges, and the degree of particle agglomeration and sizes varies with the Pt:C ratio. Several studies have shown that the ionomer distribution throughout the CL strongly depends on the overall ionomer content.^{30,171,173,201} The Pt:C ratio also plays a significant role in the ionomer distribution. As shown in Figure 37, the results suggest that lower Pt:C ratio promotes a more uniform distribution of the ionomer throughout the CL structure, providing a higher coverage and enabling the exposure of a higher inter-agglomerate pore volume (Figure 36B). Lower Pt:C ratio, on the other hand, can promote ionomer accumulation on the >20 nm mesopores and decreasing the Pt surface coverage.



Low Pt:C ratio



High Pt:C ratio

Figure 37. Schematic illustrating Pt and ionomer distribution as a function of Pt:C ratio at a fixed I:C ratio illustrating Pt particle (red), carbon agglomerates (black) and ionomer (blue) distribution.

4.3 Water Uptake

The water sorption isotherms obtained with the CL samples, along with previous results for 3M 825 EW membrane are shown in Figure 38. The CL water uptake isotherms are similar in shape to that corresponding to the 3M bulk membrane and previous results from Nafion reports.^{184,202} The 3M bulk membrane exhibits higher over the entire water vapor activity range, when compared to the 30:70 and 50:50 Pt:C CL samples; these results are in agreement with previously reported data on CL water uptake.^{202,203} Swelling ($\lambda=6$) behavior is only observed in the CLs at high RH (>0.95), this swelling attenuation in the CL samples agrees with previous observations in recast ionomer films.^{177,204–208} A decrease in water uptake in these thin ionomer films have been associated with an increase in the Young's modulus caused by polymer confinement²⁰⁵ or, as also likely, the effect of interaction of the ionomer with support.

On the other hand, the 70:30 Pt:C ratio sample exhibits higher water uptake values than the 30:70 and 50:50 Pt:C ratio CL materials over the entire water vapor activity range and it also exhibits larger swelling at a lower RH. Previous studies have shown a strong influence of the presence of Pt on the water uptake by the CL.^{202,209} A higher Pt:C ratio involves the presence of larger Pt particle sizes and degree of agglomeration (Figure 30), which can accentuate this effect. The higher uptake observed in the highest Pt:C ratio can be explained by two factors: (i) a higher primary pore (2-20 nm) volume (Figure 36B), where capillary condensation of

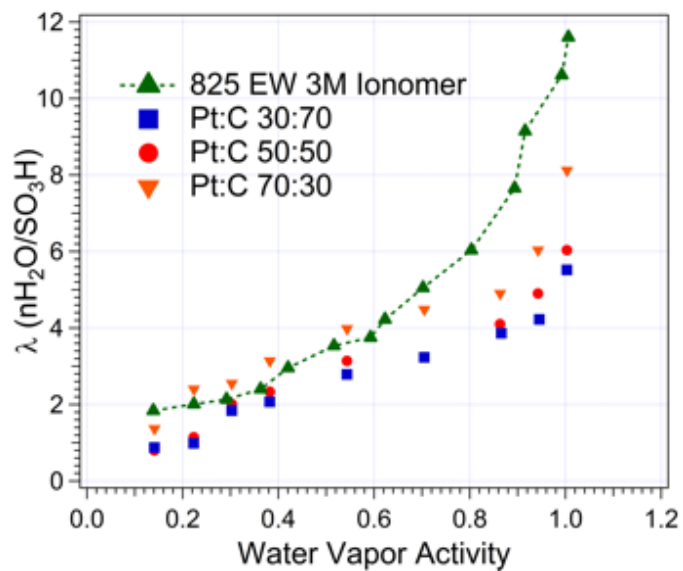


Figure 38. Water uptake isotherms for the set of CLs (30:70, 50:50 and 70:30 Pt:C ratios). The isotherm for bulk 825 EW 3M ionomer obtained in previous studies have been included as a reference.²⁵⁷

water can take place,^{5,30,167} and (ii) the larger ionomer agglomeration suggested by the BET characterization (Figure 36) enables more bulk-like ionomer behavior. Overall, we note that the water uptake data suggest that higher Pt loading is associated with weaker interactions, leading to a suggestion that the ionomer-carbon interaction is a quite significant factor.

4.4 Catalyst Layer Proton Conductivity

The σ_{CL,H^+} measurements are shown in Figure 39, along with the bulk 825EW 3M ionomer results calculated elsewhere.^{184,210,219–224,211–218} The CL samples and the bulk membrane exhibit a similar trend with RH: the proton conductivity increases with hydration, as reported in the literature for Nafion membranes¹⁸¹ Overall this reflects, with increasing hydration, the gradual loosening of the proton interaction with sulfonate groups in which the environment of the proton hydrate ‘complex’ evolves from contact ion pairs to solvent-separated ion pairs and then to fully dissociated protons moving in a water-like medium. In studies of membranes, this change in environment is associated with a variation in the proton transport mechanisms with the humidity level. At lower RH, in the absence of a fully developed hydrogen-bond network, the vehicular mechanism prevails.^{225–227} When the RH increases, bulk water phase formation throughout the ionomer promotes proton transport through structural diffusion (Grotthus hopping). In contrast to the vehicular mechanism, structural diffusion is not limited by the

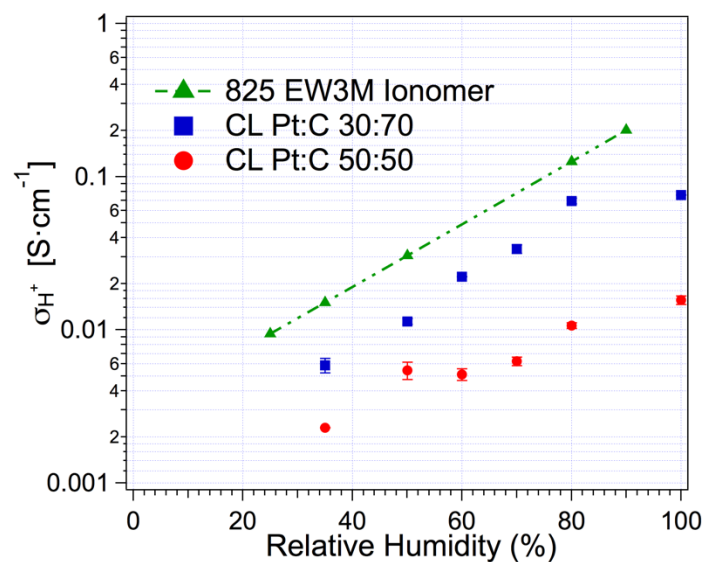


Figure 39. Proton conductivities measurements for the 30:70 and 50:50 Pt:C ratio CLs as a function of cathode relative humidity. The behavior for bulk 825 EW 3M ionomer obtained in previous studied have been included for comparison purposes.²⁵⁷

translational movement, which results in faster proton conduction.^{177,178,228} As always for macroscopic measurements, all environments and mechanisms may be locally present and it is the difference in contribution of a given aspect to a population-weighted average that is actually observed.

Similar to previous reports on Nafion thin-film samples, the CL samples exhibit a lower proton conductivity when compared to the bulk 3M membrane.^{178,181,210,229} This trend is ascribed to confinement and substrate interaction effects.²³⁰ In the CL ionomer, the nature of the ionomer-Pt and ionomer-carbon interactions determine the resultant ionomer nanostructure (i.e. ordering, thickness etc.), affecting the water content and thereby transport properties of ions and water within it.

Among the CL samples, the lowest Pt:C (30:70) ratio exhibits higher σ_{CL,H^+} values (Figure 39). This result coincides with the physicochemical characterization result: the lower secondary pore volume obtained with the 30:70 Pt:C ratio sample suggests lower ionomer accumulation in the pores and a more homogeneous ionomer distribution throughout the CL.

Thus, the increased ionic conductivity observed in CL samples with low Pt:C ratios can be related to the more continuous ionomer network that also promotes the structural diffusion mechanism. This is consistent with the previous findings of Sun and Zawodzinski.¹⁸⁸

4.5 Cyclic Voltammetry (CV) Experiments

The oxidation branch of the CV results for the 30:70 and 50:50 Pt:C ratio CL samples are shown in Figure 40. The hydrogen desorption charge density was used to calculate the ECSA of the fuel cell electrode. The ECSA calculations were 69.0 and 62.8 $m_{Pt}^2 \cdot g_{Pt}$ for the 30:70 and 50:50 Pt:C ratio samples, respectively.

Although the 50:50 Pt:C ratio sample presented a lower particle size, the 30:70 Pt:C ratio sample exhibited a higher ECSA when compared to the 50:50 Pt:C ratio electrode. This can be associated to the higher degree of agglomeration observed in the 50:50 Pt:C ratio sample, which can be detrimental to the exposed surface area.

4.6 PEMFC Performance Evaluation

Figure 41 shows a representative polarization curve for 30:70 Pt:C CL in H₂/air. At the lower overpotential range (cell working potential > 0.7V), lower RH polarization curves exhibited the lowest current output. This result coincides with the observed ionic conductivity trend, which showed a direct proportionality relationship with RH. Since the proton transport is confined to the hydrated sites, both the ionomer inside the CL and the proton exchange membrane offer lower proton conductivity at lower RH level.

However, as the overpotential increases (cell working potential < 0.7V), cells at lower RH levels (<50%) reach a larger current output than those operating under

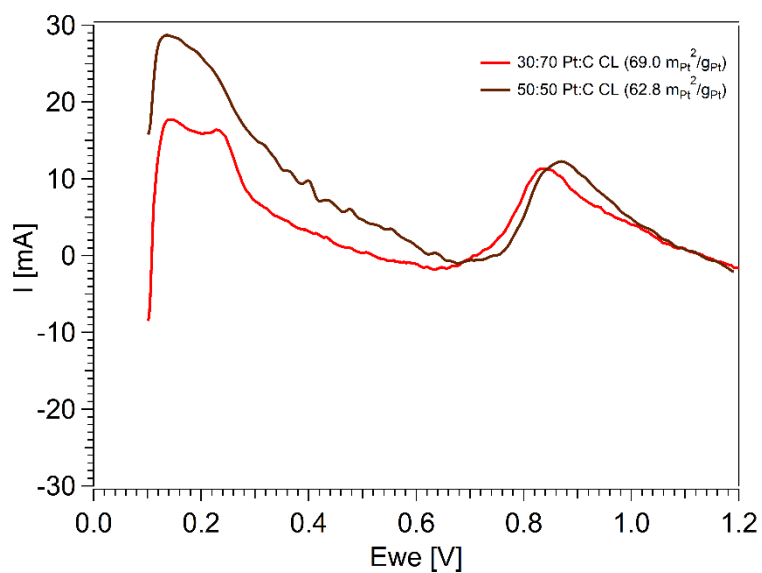


Figure 40. Cyclic voltammograms of the 30:70 and 50:50 Pt:C ratio PEMFC catalyst layers. Conditions: Scan rate = 20 mV⁻¹; Cell: 80°C; 100% RH anode/cathode; 2 atm.

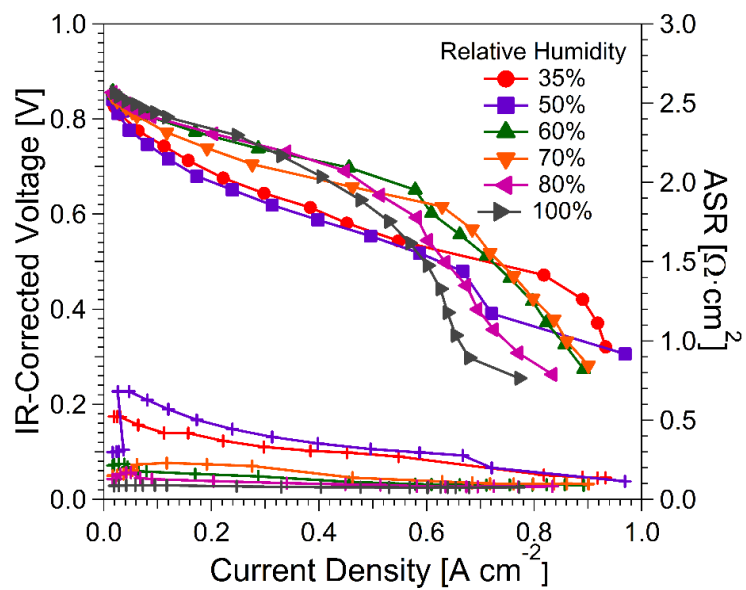


Figure 41. H₂/air polarization curve and ASR of the 30:70 Pt:C free-standing electrode. The curves were obtained at 2 atm backpressure and the cell temperature was held at 80°C.

high RH. This effect can be associated with water formation at higher overpotential, which can provide a pathway for proton transport at low RH. At high RH, on the other hand, water formation could potentially cause flooding in the cell, hindering gas transport and becoming detrimental to the current output. The effect of water production can be further confirmed by the drop of area specific resistance (ASR) along with the decrease of the working potential, which is especially pronounced amongst the lower RH level cells.

In general, the cell optimum performance occurs at the 35%-70% RH range. Compared to typical Nafion CLs' peak performance at 100% RH, the 3M ionomer allows the cell to operate effectively under dryer conditions. Also, the improvement of performance in the 35% RH cell indicates that the 3M CLs are sensitive to the water content inside the operating system. This is further justified by the fact that the cells operating at high RH levels (>80%) suffer sudden current decrease in the mass transfer region.

After comparing the polarization curves of the three different Pt:C ratio CLs (Figure 42B) at 60% RH, a significant difference was observed particularly at low current density values (kinetic region). The 30:70 Pt:C ratio sample exhibits nearly a 100% increase in current density at 0.85 V over that of the 70:30 Pt:C ratio sample ($j_{70:30\text{Pt:C}}: 0.0697\text{A}\cdot\text{cm}^{-2} < j_{50:50\text{Pt:C}}: 0.0837\text{A}\cdot\text{cm}^{-2} < j_{30:70\text{Pt:C}}: 0.126\text{A}\cdot\text{cm}^{-2}$ at 0.85 V). This outcome agrees with the ECSA calculations obtained from the CV measurements (Figure 40). Furthermore, the 30:70 Pt:C ratio cathode prevails

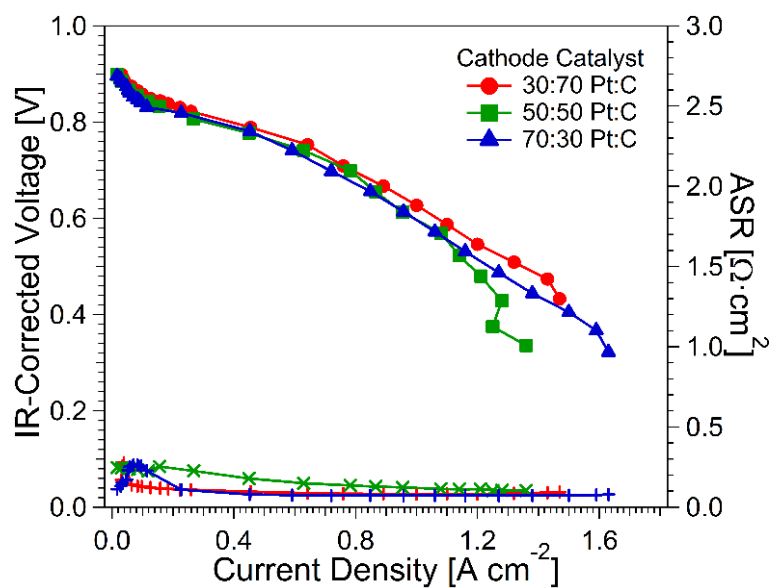


Figure 42. Polarization Curves of the free-standing CLs with different Pt: C ratios under H_2/O_2 operation at 60% RH. The curves were obtained at a 2 atm backpressure and the cell temperature was held at 80°C.

over the whole current density range. This agrees with the characterization results: the 30:70 Pt:C ratio exhibited a lower degree of Pt agglomeration and Pt particle size and higher proton conductivity over the whole RH range.

Furthermore, the cell reaches a rather low limiting current ($\sim 1.5 \text{ A} \cdot \text{cm}^{-2}$ under H_2/O_2 and $\sim 0.8 \text{ A} \cdot \text{cm}^{-2}$ under H_2/air). This implies that the oxygen transport impedance at lower current density is more pronounced than expected. There are two possible reasons for such issues. On one hand, given that the CL ionomer reaches its swelling point at a lower overpotential, the excessive water could not attach onto the 3M ionomer but linger in the pores structures. Without efficient removal, the “trapped” water could greatly hinder oxygen from reaching the reaction sites, therefore causing the increasing mass loss. On the other hand, the presence of the microporous layer (MPL) in the GDL can also affect mass transport. Previous studies have shown water transport is greatly influenced by MPL parameters, such as thickness, pore size, porosity distribution and hydrophilicity.^{5,30,167} As described in the experimental section, the cathode electrode in this study was hot pressed onto the MPL first, then hot-pressed onto the Nafion membrane. These two hot-pressing processes could potentially alter or damage the MPL structure, affecting the parameters mentioned above. Alternatively, water accumulation at the MPL/CL interface can also occur, hindering gas mass transport to the CL.

To summarize this discussion, a significant influence of Pt particles and their size on the CL structure and properties was observed. In general, all CLs showed a

significant deviation from the bulk-like ionomer behavior. Lower Pt content resulted in a lower Pt particle size, higher inter-particle distance, and a larger secondary pore (>20 nm) volume. The latter has been associated with a more homogeneous ionomer distribution, given that the I:C ratio was fixed for all CLs in this study. The lowest Pt:C ratio, consequently, provided higher proton conductivity and higher PEMFC performance. Higher Pt content, on the other hand, presented a significantly higher Pt particle size and degree of agglomeration. In terms of pore network, the 70:30 Pt:C ratio CL displayed a reduction in the secondary pore volume, but a slightly higher primary pore volume. Pulling this together, the highest performance in fuel cell tests was most strongly correlated with the highest volume of macropores and the highest observed proton conductivity.

4.7 Conclusions

Machine-prepared CLs with different Pt:C ratios were characterized and tested in a PEMFC. In all samples, the images showed a preferential Pt deposition on the graphitic carbon structure defects, leading to a heterogeneous particle distribution throughout the CL. The highest Pt:C ratio exhibited a higher Pt particle size and degree of agglomeration. Although all samples exhibited a similar Pt particle size distribution behavior, significant differences were observed in terms of pore size distribution. For instance, the lowest Pt:C ratio (30:70) exhibited a higher volume of secondary pores. Furthermore, this sample exhibited a higher proton

conductivity and superior PEMFC performance. Such behavior was associated with a more homogeneous ionomer distribution throughout the CL.

Chapter 5

^{19}F NMR STUDIES OF 3M IONOMER ADSORPTION ON CARBON SUPPORTS AND PT/C CATALYSTS

A version of this chapter was originally published by N. M. Cantillo, L. Li, J. Peng, G. A. Goenaga, and T. A. Zawodzinski:

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Data acquisition for this article was performed entirely by Nelly Cantillo. The conception and design of the study was done by Nelly Cantillo in conjunction with Dr. Gabriel Goenaga, and Dr. Thomas Zawodzinski. Dr. Luyue Li cooperated with fuel cell setup and experiments. And Dr. Jing Peng cooperated with NMR experiments.

Data analysis was performed by MSc. Nelly Cantillo and Dr. Thomas Zawodzinski. Cantillo prepared the draft of the manuscript and along with Dr. Thomas Zawodzinski revised the manuscript thoroughly before submission. Approval of the final version of the manuscript to be published involved all authors.

Abstract.

In this study, the interactions between 3M 825 equivalent weight (EW) ionomer and different carbon supports were studied. The adsorption of ionomer on a series of Pt:C (0:100, 30:70, and 50:50) ratios using Vulcan XC-72 Carbon as support were evaluated to further understand this interaction. The adsorption properties of water-dissolved 3M 825 EW ionomer on both the carbon supports and the series

of Vulcan-supported platinum catalysts were studied with Inductively Coupled Plasma Optical Emission Spectrometry. Progress toward developing methods for studying polymer adsorption onto supports using ^{19}F Nuclear Magnetic Resonance Spectroscopy is also reported. A detailed structure characterization of the pristine supports and catalyst materials was achieved through Brunauer-Emmet-Teller nitrogen adsorption-desorption, transmission electron microscopy, X-ray diffraction and Raman Spectroscopy. The adsorbed ionomer structure was also explored through Solid State NMR.

5.1 Introduction

As discussed in Chapter 4, conventional CLs involve an ionomeric component to provide a proton-conducting pathway to the catalyst sites. Such CLs are commonly formed from a mixture of the components, also known as catalyst ink, which comprise the carbon-supported catalyst (e.g. Pt/C) and PFSA ionomer, dispersed in an aqueous solvent. The resulting CL structure is influenced by the dispersion of the components in solution which, in turn, depend on the dispersion medium.

Different CL fabrication techniques, however, require dispersion media with specific characteristics. Fabrication techniques such as hand-painting, screen-printing or roll-to-roll coating require a viscous ink with a high solid content (>5 wt. %) and high-boiling-point additives.¹⁶⁵ In contrast, the spray-coating technique requires a lower solid content (<2 wt. %) and a volatile medium, typically using a

water or alcohol solution. The early work of Aldebert et al. found a significant influence of the nature of the solvent on the morphology of Nafion in solution. The SANS spectra of Nafion solutions in water and ethanol evidenced significant differences in the polymer morphology.

PFSA ionomers are composed of a PTFE backbone and a perfluorinated pendant side chain with an ionic group and the associated counterion (Figure 2). The structural difference between the backbone and the side chain results in microphase separation between the hydrophobic matrix and the hydrophilic ionic domains.¹⁸¹ Such separation, which is accentuated by solvation, is essential for the proton conduction capabilities of this type of polymers.

In this study, CLs containing 3M ionomer were studied. The 3M ionomer contains a shorter side chain (lower formula weight of the repeat unit) as indicated in Figure 2. Therefore, at a given EW, such an ionomer has a higher content of PTFE backbone, which improves the mechanical properties (higher T_α) and leads to a higher proton conductivity at higher temperature and drier operation conditions. Recently, an ionomer having the same chemical structure as the 3M PFSA has been studied by Asahi Kasei.²³¹ A comparison between Nafion (EW950) and 3M ionomer (EW800) showed that the 3M polymer had a higher T_α and higher conductivity and thermal stability in TGA tests under both air and Argon.

5.1.1 PFSA Morphology

Over the last decades, a variety of studies using small- and wide-angle scattering with X-rays and neutrons have attempted to understand the molecular/supramolecular organization of PFSA ionomers over a wide range of physical states. Several models have been proposed in an attempt to explain the obtained data.^{176,181,232–235} Here we will discuss the most representative models over time.

5.1.1.1 Cluster-Network Model

Extensive work in the 1970's and early 1980's focused on the elucidation of Nafion's morphology.^{232–235} Based on SAXS and wide-angle XRD, Gierke et al. concluded that ionic clustering, understood as hydrated ionic aggregates, occurs upon Nafion hydration.^{232,233} This conclusion was drawn from their study over a wide range of Nafion EWs in the unhydrolyzed sulfonyl fluoride acid form, the hydrolyzed sulfonic acid form, and the neutralized metal sulfonate form. The scattering peak observed at $\sim 1.6^\circ 2\theta$ with the hydrolyzed sample was associated with the formation of ionic clusters within a semicrystalline matrix. These results, along with TEM imaging, motivated the hypothesis that the adsorbed water phase distributes into an approximately spherical inverted micellar structure throughout the ionomer matrix with the ion exchange sites located near the interface. Figure 43 shows a representation of the cluster-network model with a depiction of the

effect of hydration. At low water content, isolated spherical clusters (~1.5 nm diameter) are separated by an inter-cluster distance close to 2.7 nm.²³⁶ Upon swelling, cluster diameters can increase up to 4 nm leading to percolation.

It is important to note, however, that this model was not proposed as a definitive description of Nafion's morphology.²³² Conversely, it constituted an early attempt to describe the spatial distribution of inverted micelles clusters for simple space-filling calculation purposes.

5.1.1.2 *PFSA in solution: Rod-like Elongated Polymer Aggregates*

Reports by Loppinet and Gebel suggested that PFSA ionomer solutions could be described as a colloidal structure in rod-like particles.^{237–239} These studies were performed through the evaluation of Nafion (EW=1100) solutions in polar solvents (e.g. alcohols, amides and water) by SAXS and neutron scattering. The scattering curves exhibited a pronounced peak, whose intensity depended on the polymer concentration.²³⁹ This peak was, consequently, associated to interference between the scattering objects due to electrostatic repulsions. A cubic phase of rods (Figure 44) was found to be the best model for the obtained data. The nature of the solvent showed to have a strong influence on the diameter of the individual

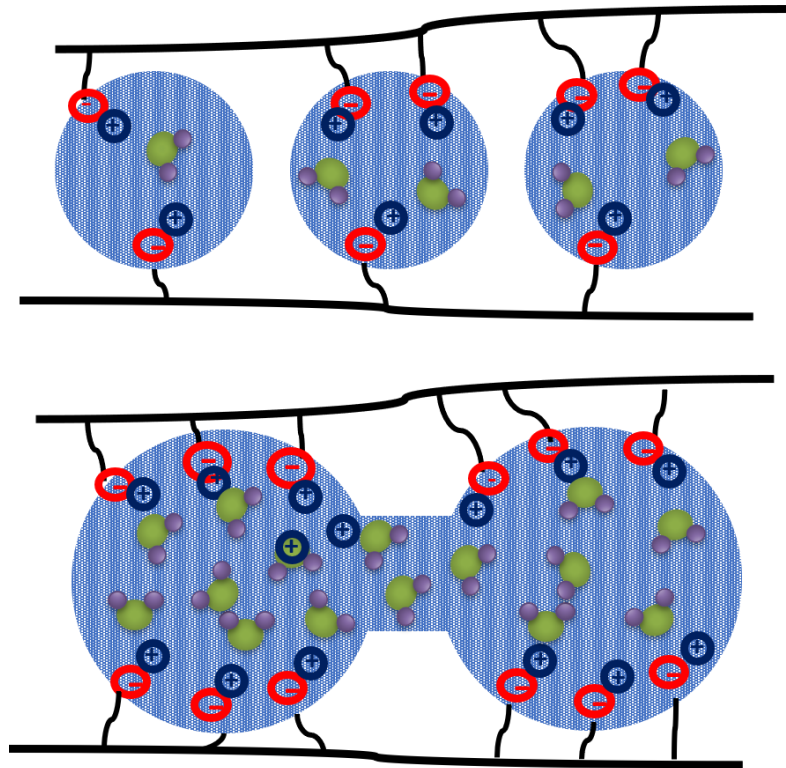


Figure 43. Cluster-network model scheme at low (top) and high (bottom) water uptake proposed by Gierke et al.^{232,233}

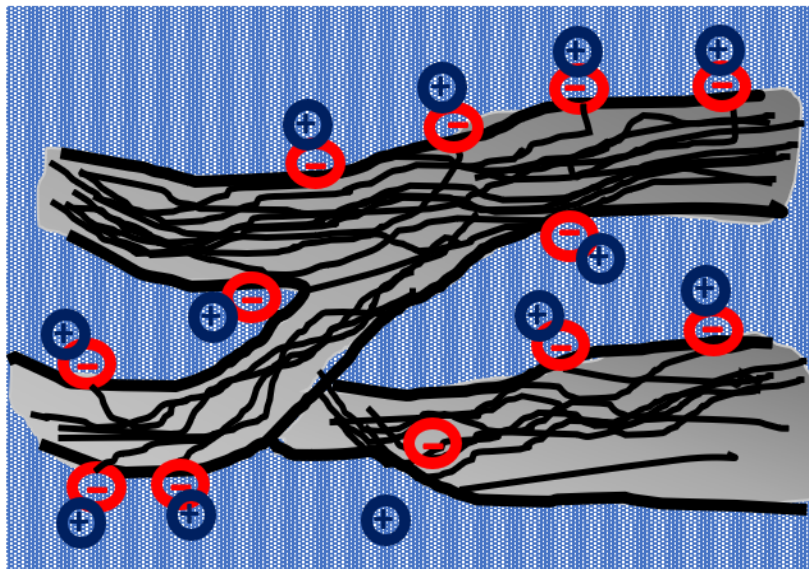


Figure 44. Rod-like elongated polymer aggregates scheme representing ionomer distribution in solution as described by Loppinet and Gebel.^{237–239}

rods. This influence was associated to differences in the dielectric constant. In an alcohol such as ethanol ($\epsilon_r = 24$), the electrostatic repulsion between charges is expected to be stronger than in water ($\epsilon_r = 80$), causing the system to be more elongated. Further work, however, showed that an increase in the dielectric constant promotes the existence of a local order but does not have a significant influence on the rod diameter.²³⁸

5.1.1.3 PFSA Thin-Films

As discussed above, extensive studies have focused on the properties and morphology of “bulk” PFSA ionomer membranes (25-175 μ thickness). Recently, PFSA ionomer thin films studies have attracted considerable attention as an attempt to understand the morphology of the ionomer in the CL (which is believed to form a 1-3 nm layer surrounding carbon agglomerates) and the interfaces formed within the electrode. In the thin-film regime (<1 μ m thickness), the properties of the ionomer are affected by the thickness and the interaction with the substrate.^{205,206,209,229,240,241} Surface interactions and confinement can cause anisotropy in domain orientation, posing significant limitations to self-assembly.¹⁸¹

In general, PFSA thin films are fabricated by casting a diluted ionomer dispersion onto a substrate by different methods (spin-casting, self-assembly, drop-casting, etc.).^{177,181,205,206} Most of these studies have been performed with Nafion. Significant reduction in transport properties such as ionic conductivity and water

uptake have been observed with thin-film thicknesses below 100 nm.^{209,241} Recently, Kusoglu et al investigated the morphology of PFSA ionomers of various chemical structures (e.g., side chain length, EW) over a wide range of length scales (from bulk with thicknesses $>10\mu\text{m}$ to thin films <100).²¹⁰ In particular, GIXAS was employed to explore the nanostructure of both Nafion and 3M ionomer thin film over a silicon substrate. All ionomer films exhibited a scattering half-ring, which is an indication of phase separation of hydrophilic domains and hydrophobic matrix. Nevertheless, Nafion and 3M ionomer exhibited different features in terms of peak shape and a slightly more anisotropic scattering ring in the 3M ionomer case.²⁰⁹ The authors associated these differences to two effects: higher swelling and fraction of ionic group in the 3M ionomer (lower EW) at a given RH, which results in better phase separation, and a higher tendency of the 3M thin films to align the backbone chains to the substrate due to the shorter-side chain.

To investigate the nanostructure anisotropy, the scattering intensity was analyzed as a function of the azimuthal angle and the FWHM of the ionomer peak was calculated for the different ionomers at different thicknesses. Several thickness regimes were identified through this analysis: a bulk-like behavior (>100 nm), a thin-film regime (50-60 nm) where reduced swelling and anisotropic nanostructure results from the confinement effect and an ultrathin film regime (<20 nm) with dispersion-like behavior.

5.1.2 *PFSA Thin Film Interactions*

Several studies of PFSA ionomer thin films over a variety of substrates (i.e. SiO₂, Pt, Au, etc.) have been published in the recent years.^{177,240–243} The data obtained have enabled the study of the interactions of such thin films upon adsorption on the substrate. The nature of the substrate has shown to be a primary influence the morphology of the adsorbed ionomer, particularly at the ionomer/substrate interface. Of course, this calls into question transferring these conclusions to real systems.

Neutron reflectometry (NR) has been used to explore the orientation and spacing of the nanodomains at and below the interface.^{206,242,243} Dura et al. employed this technique to determine the nm-scale structures of both water and Nafion in spin-coated Nafion films over different substrates (SiO₂, Pt, Au) and at different hydration conditions.²⁴³ The substrate surfaces were subjected to UV ozone cleaning and 60°C annealing prior to the coating. A multilamellar nanostructure at the ionomer/SiO₂ interface was proposed to fit the data. The lamellae in this model consists of three water-rich layers alternating with two Nafion-rich layers with the water content decaying from nearly 100 vol.% (adjacent to the surface) to ~60 vol.%. This arrangement was associated with induced ordering of the rod-like aggregates or lamellae observed in SAXS and SANS, where the first Nafion layer would consist of closely packed ribbons or lamellae oriented parallel to the substrate.^{237,239,244} On hydrophilic surfaces such as SiO₂, ionomer adsorption can

occur via interaction with the SO_3H groups (Figure 45), whereas hydrophobic substrates may interact with the nonpolar CF-rich chains.^{181,242,245–247}

In contrast, data obtained using Pt and Au as substrates did not conform to the multiple lamellae model. Measurements on these substrates suggest the presence of a thin, partially hydrated single interfacial layers, whose thickness is reduced upon dehydration. This behavior was associated to a lower affinity of the Pt and Au substrates to the sulfonic acid/water phase compared to the more hydrophilic SiO_2 . This conflicts, however, with the reports published by Mohamed et al. and Ohira et al., which suggested that adsorption on Pt substrates is significantly favored by the interactions between the sulfonic acid group and the polar groups present in hydrophilic substrate.^{247,248} The former compared Nafion adsorption on silicon (Si), GC and platinum/silicon (Pt/Si) substrates through XPS, AFM and contact angle measurements.²⁴⁷ The surface of the ultrathin Nafion film on Si was found to be highly hydrophilic and a high concentration of oxygen was observed by XPS characterization of the film surface away from the substrate interface. These findings were ascribed to repulsion of the SO_3H groups by the hydrophobic native oxide layer on the untreated Si substrate, displacing them towards the surface of the ionomer film. In contrast, Pt/Si exhibited a lower extent of SO_3H 'enrichment' in the ionomer surface, which was associated to a stronger $\text{SO}_3\text{H}/\text{PtO}$ interactions. The existence of such interaction, nevertheless, has been further confirmed through electrochemical characterization.^{249,250}

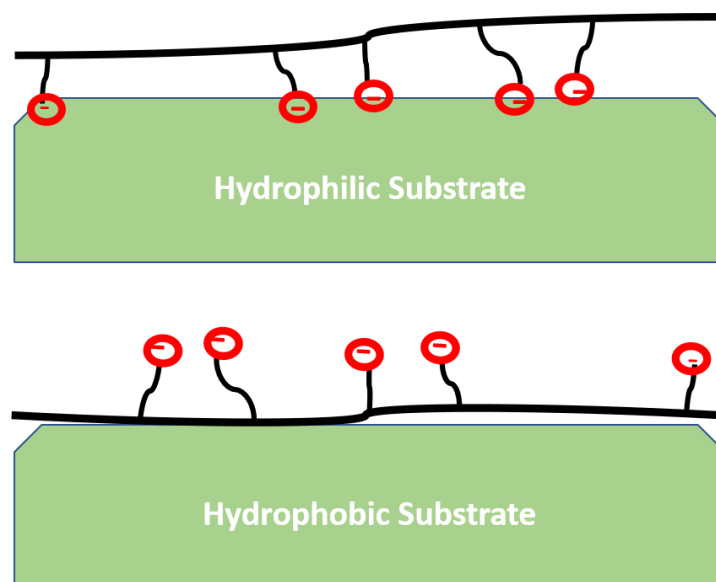


Figure 45. Schematic representation of Nafion adsorption scheme on substrates with different wetting properties.

5.1.3 *Thin Film Properties*

Reduction in transport properties have been observed and these are typically explained as a consequence of structural changes that the PFSA ionomer undergoes in the thin film regime. For instance, studies have found that ionomer thin films exhibited significantly lower water-sorption rates when compared to bulk ionomer membrane, which has been ascribed to the interfacial nature of these films.^{202,207,209} In this context, 'interfacial nature' refers to a strong influence of the substrate on the nanostructure of the films.

Shim et al. established that the conductivity- λ relationship obtained by Zawodzinski et al.¹⁸⁴ for bulk membranes can be extended to Nafion films with thicknesses as low as 25 nm.²²⁸ This finding allowed the correlation of the low conductivity values obtained with thin films to a reduction in the water uptake.^{177,241} Confinement effects, however, might gain more relevance when the thickness approaches the characteristic domain size of the ionomer (<5nm). In the electrode structure, TEM-based measurements and theoretical calculations have resulted in 1-3 nm thickness values.^{5,16}

Furthermore, oxygen mass transport resistances in ionomer thin films have shown a significant reduction.^{249,251} Kudo et al, for instance, evaluated oxygen transport resistances of Nafion thin films through the measurement of the oxygen flux through the film on the coated Pt microelectrode as diffusion limited current density

for an ORR.²⁴⁹ The authors found a dependence of the O₂ permeation reduction on the thickness of the film. It was claimed that this is an effect of polymer-surface interactions, especially at the Pt/ionomer interface.

5.1.4 Summary

PFSA thin film research has suggested the existence of three regimes: (I) a bulk-like regime (>100 nm), (II) a thin-film regime where rearrangement of the structure occurs causing reduction of transport properties such as water uptake and conductivity, and (III) an ultrathin film regime (<20 nm) with dispersion-like behavior characterized by reduced phase separation between the hydrophilic and hydrophobic domains. Factors such as EW and the nature of the substrate have shown to influence thin film structure arrangement. Reducing EW seems to result in a better phase separation and domain orientation, as shown by comparisons between 3M and Nafion ionomers.

Here, the interactions of standard carbon support structures and carbon-supported Pt materials with 3M ionomer were studied with adsorption isotherm in aqueous solution based on ¹⁹F NMR and ICP-OES. The adsorption parameters were analyzed in light of the structure of the supports and Pt content. We describe an analysis of the adsorption the results of applying several physical characterization methods to explore CL structure and interactions with 3M 825 EW ionomer.

Furthermore, SSNMR results of the adsorbed ionomer are presented. These studies provide a first step toward understanding the behavior in real systems.

5.2 Transmission Electron Microscopy

The TEM micrographs for the Vulcan, Acetylene Black and BP2000 supports are shown in Figure 46. These materials represent supports with different surface areas and graphitic character. While the V72, one of the most common electrode supports, depicts a porous, turbostratic material with a mid-range surface area; the BP2000 is considered a high-surface-area carbon (HSAC). The acetylene black structure, on the other hand, corresponds to a highly graphitized low surface area carbon (LSAC). The graphitic structure of this material can be easily appreciated in Figure 46 (upper right), where the characteristic facets of graphitic carbon can be observed. A diagram of the structure of these distinct carbon supports is shown in Figure 47, illustrating nanoparticle dispersion.²⁵²

Figure 48 shows the micrographs of the 30 and 50% Pt/V72. The average Pt particle size is 1.6 and 1.2 nm for the 30% and 50% Pt/V72 samples, respectively. However, the 50% Pt/V72 sample exhibits a higher degree of Pt particles agglomeration, exposing less bare carbon surface area than the 30% Pt/V72 sample.

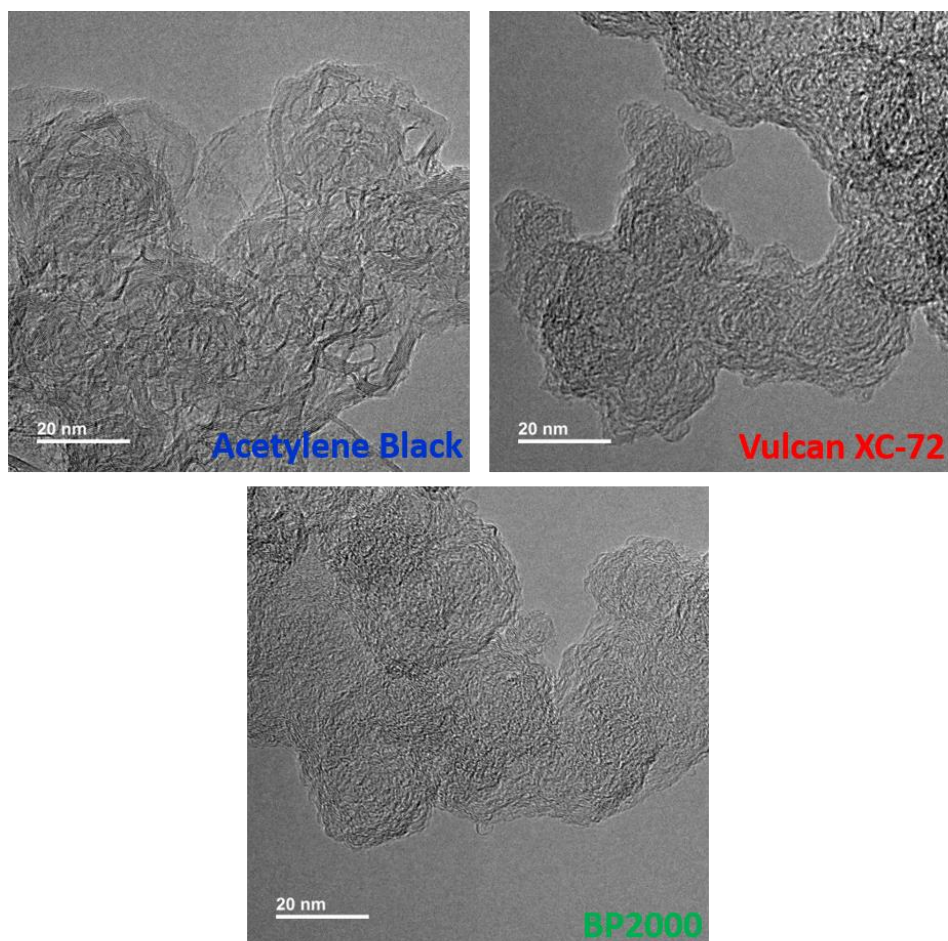


Figure 46. TEM images of the Acetylene Black, Vulcan XC-72 and BP2000 illustrating the different carbon structures. Acetylene black exhibits a graphitic structure, while Vulcan and BP display a mesographitic or turbostratic structure.

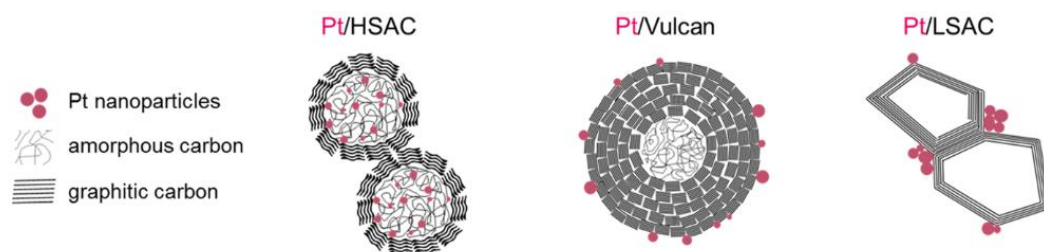


Figure 47. Illustrations of the structure of various carbon supports and Pt nanoparticle dispersion: Pt/HSAC, Pt/Vulcan, and Pt/ LSAC (left to right) based on HRTEM/STEM observations.²⁵²

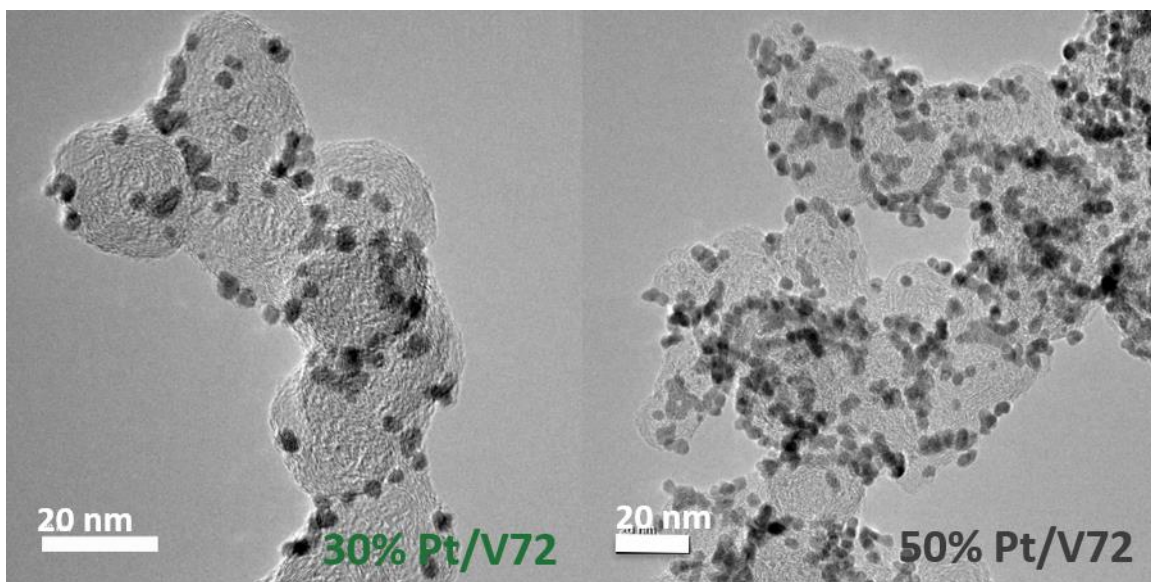


Figure 48. TEM images of the 30 and 50% Pt/V72 showing a significantly different Pt particle distribution throughout the Vulcan carbon support.

5.3 Surface Area and Pore Size Distribution

Figure 49 illustrates the gas adsorption isotherms obtained for the carbon samples: Vulcan XC-72, acetylene black, KJB EC600JD and BP2000. All these isotherms are type II adsorption according to the IUPAC classification.³² This suggests that the samples contain macropores (>50 nm) where monolayer and multilayer nitrogen adsorption can take place. At very low relative pressure (P/P_0), the steep rise indicates the presence of micropores (<2 nm) and the monolayer coverage is the dominant process. As the partial pressure increases, the low-relative-pressure (LRP) inflection point indicates the complete filling of micropores and the multilayer process proceeds. In this region, the mesopores in between the Pt/Carbon agglomerates are filled. As the partial pressure reaches unity, the sharp increase is due to the rapid filling with capillary condensation. After the pressure saturation is reached, desorption is carried out.

All samples exhibited hysteresis. According to the IUPAC classification, the obtained isotherms follow the behavior of the H3 type hysteresis. This shape implies two things: first, the existence of aggregates of particles that form pores with non-uniform size and/or shape; second, the limited volume of large pores trapped between smaller pores.^{253,254}

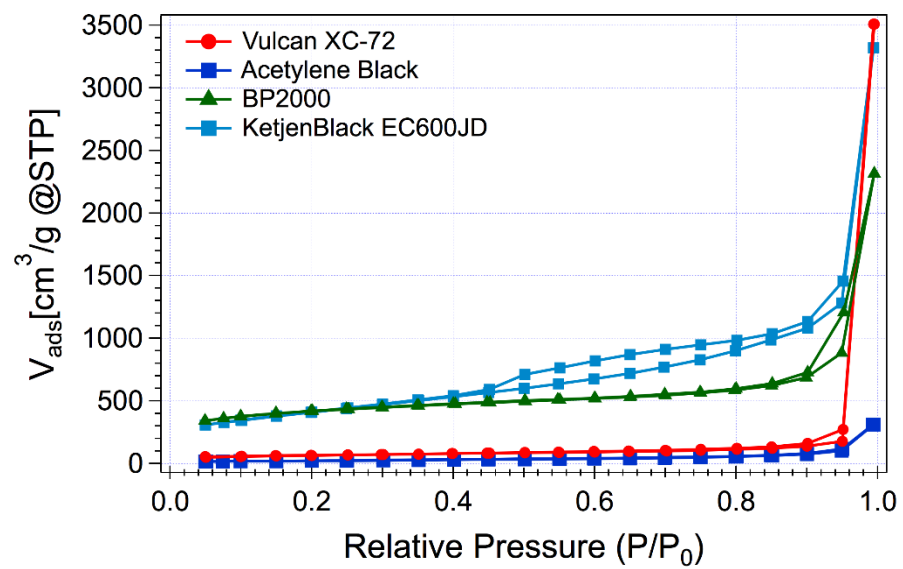


Figure 49. N_2 adsorption/desorption isotherms for the Vulcan XC-72, Acetylene Black, BP2000 and KJB carbon samples.

For the total surface area measurement, BET theory was used to analyze the data. Table 8 shows the surface area values. As expected, KJB and BP2000 exhibit high BET surface area values (over $1000 \text{ m}^2 \cdot \text{g}^{-1}$), whereas acetylene black exhibits a low value (below $100 \text{ m}^2 \cdot \text{g}^{-1}$).

Furthermore, the PSD was analyzed using the BJH approach.²⁵³ The PSDs of all the types of carbon was estimated from the desorption branch of the isotherms, given that this branch exhibits lower relative pressure, resulting in a lower free energy state and therefore is closer to true thermodynamic stability.²³ The result is shown in Figure 50 (A). Although all samples exhibit a similar trend: a sharp peak at a $\sim 4 \text{ nm}$ pore diameter, and a wide peak around 100 nm pore size, the KJB sample exhibits a significantly higher pore volume in the primary pore region. To visualize this effect, the cumulative pore volume was calculated for each sample in the primary pore (3-20 nm) and the secondary pore (20-200 nm) regions. The KJB sample exhibits a primary pore cumulative volume with 1-2 orders of magnitude higher than the BP, V72 and AB samples. The samples exhibit a primary pore cumulative volume in the order $V72 < AB < BP < KJB$. On the other hand, the V72 sample displayed the highest secondary pore cumulative volume. In the secondary pore region, the order is $AB < BP < KJB < V72$. The low pore volume observed with the AB sample in both regions explains the low surface area obtained with this sample.

Table 8. BET Surface area of carbon supports.

Sample	BET Surface Area [m²·g⁻¹]
Acetylene Black	78.11
Vulcan XC-72	222.87
BP2000	1379.61
KJB EC600JD	1466.17

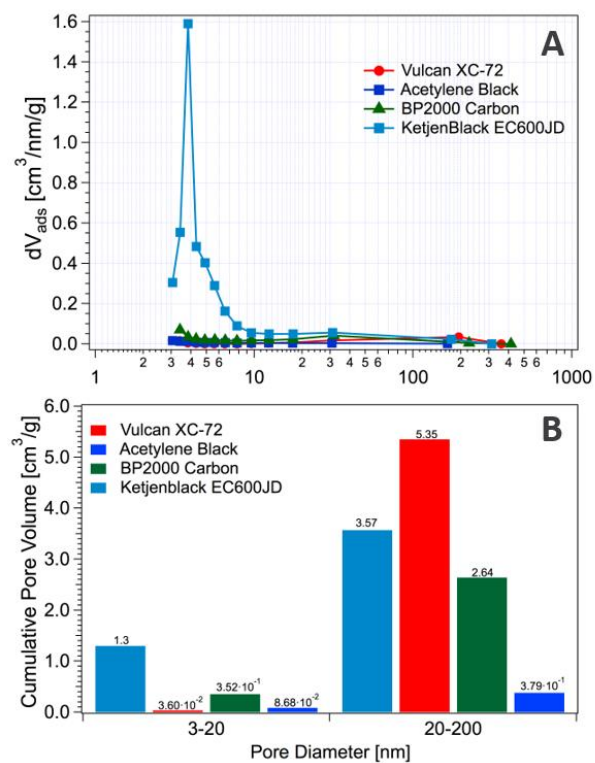


Figure 50. (A) Pore Size Distribution and (B) Cumulative Pore Volume of Vulcan XC-72, acetylene black, KJB and BP2000 exhibiting bimodal pore size distributions in all cases.

5.4 Raman Spectroscopy

The structure of the carbon materials was examined with Raman spectroscopy. First-order Raman spectra for all the materials is shown in Figure 51. All samples exhibit two characteristic peaks: the G (graphitic) band at about 1570cm^{-1} and the D (disorder) band located at about 1350 cm^{-1} .^{255,256} The G band corresponds to the E_{2g} tangential stretching mode of an ordered graphitic structure with sp^2 hybridization, while the D band is associated with disorder in the carbon structures caused by defects, the finite size of crystalline domains, sp^3 -hybridized bonds and functional groups created by oxidation.

The intensity ratio of the D over the G peak (I_D/I_G) was used to evaluate the degree of disorder of the carbon samples. Table 9 shows the estimated I_D/I_G ratios for the carbon samples. The KJB sample exhibits the highest percentage of defective over graphitic content, while the AB sample displays the lowest percentage. This agrees with the TEM images, where acetylene black displayed a graphitic structure.

5.5 ^{19}F Nuclear Magnetic Resonance (NMR) Analysis

As a first approach, ^{19}F NMR was used to characterize the ionomer in solution. Figure 52 shows an NMR spectrum of the 3M PFSA ionomer in water solution. The CF_3COOH in solution signal corresponds to the peak at -76.55 ppm , which is used for the chemical shift correction. The peaks associated with each functional group

Table 9. D and G peak intensities of the carbon samples and the respective I_D/I_G ratio.

	Acetylene	BP2000	Vulcan	KJB
D-Peak	8457.2	11060	6946.7	26806
G-Peak	15615	14635	8821.2	24618
I_D/I_G	0.54	0.76	0.79	1.09

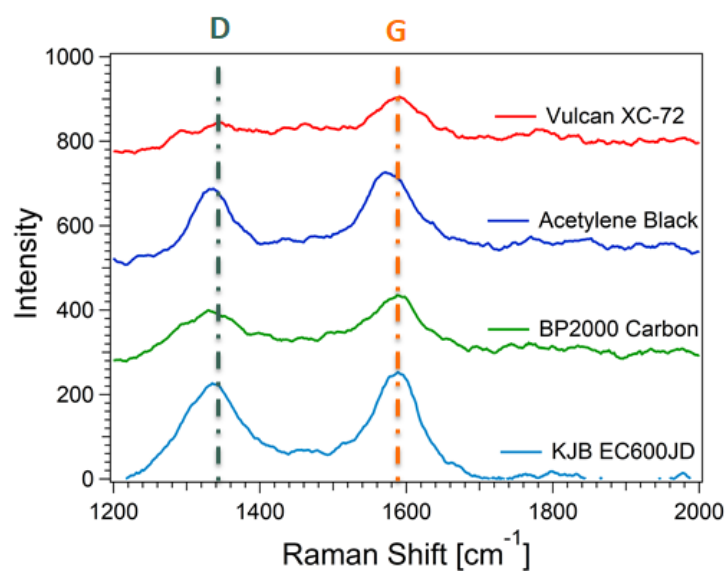


Figure 51. Raman spectra of the Vulcan XC-72 (red) Acetylene black (dark blue), BP200 (green), KJB(light blue) carbon samples.

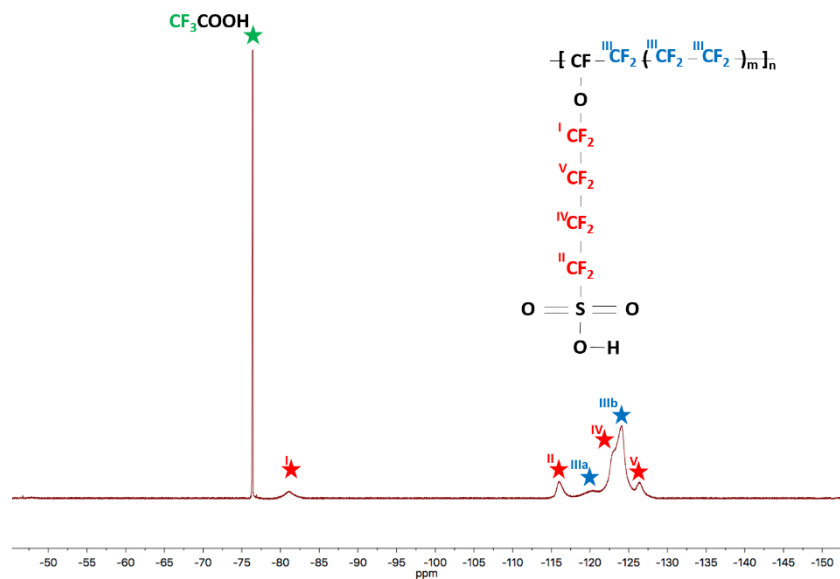


Figure 52. ¹⁹F NMR spectrum of 3M 825 ionomer and CF₃COOH solution.

in the ionomer structure are shown in Figure 52. The CF peak (around -138.55 ppm) was not identified, due to the low intensities.

Peaks III (IIIa around -119.12 ppm and IIIb around -122.79 ppm) are associated with the backbone CF₂ groups. Peaks I (around -80.32 ppm), II (around -115.82 ppm), IV (around -122.14 ppm) and V (around -125.80 ppm), on the other hand, are associated with the side-chain CF₂ groups. Overall, the most prominent peaks correspond to peak II, IIIb and IV. The ratios of these peaks (peak II and peak IIIb+IV) and the CF₃COOH peak were used for the analytical study, a similar approach to previous studies with Nafion.^{199,245,255}

3M ionomer solution concentrations showed a proportionality relation to the NMR signal ratio between the CF₂ peaks, and the CF₃COOH peak (Figure 53A). The standard curve for this ratio is shown in Figure 53B. The following linear function was obtained:

$$\frac{S_{-CF_2}}{S_{CF_3COOH}} = 1.6686 \cdot C_{3MIon} - 0.187 \quad [27]$$

Where S_{-CF_2} corresponds to the addition of the integrals of the peaks associated to the CF₂ functional group (peaks II, III^a, III^b, IV and V) and C_{3MIon} corresponds to the ionomer concentration in g·l⁻¹. In this case, the sum over several peaks was used to enhance the sensitivity of the technique. An appropriate fit ($R^2 \cong 0.9975$) was obtained by this methodology. This approach, however, presented a significant

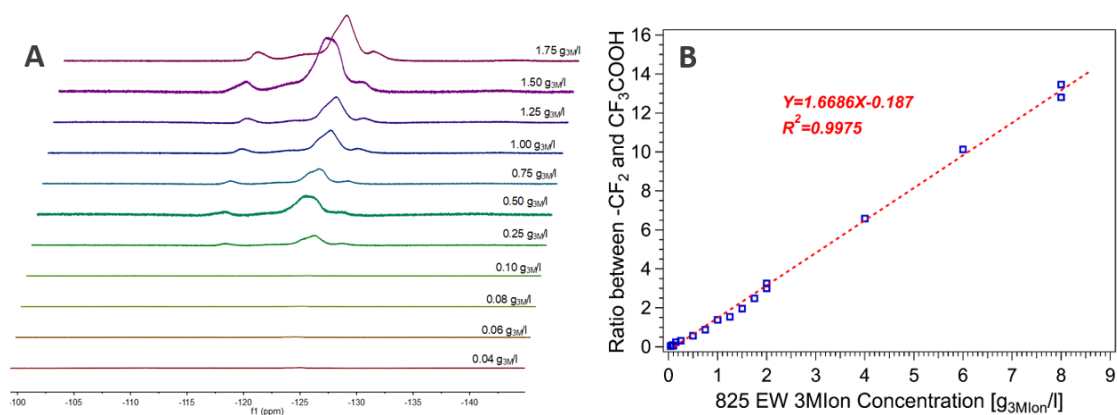


Figure 53. (A) ^{19}F NMR spectra of 3M 825 ionomer solutions and CF_3COOH solution at different 3M concentrations and (B) standard curve for 3M ionomer in water.

limitation for low concentrations given the high intercept value obtained (equation [27]). This effect is due to the effect of the noise, which is accentuated at the lower concentrations.

Figure 54 shows the adsorption behavior of both the V72 carbon and the in-house-prepared 50 % Pt/V72 sample. The Vulcan XC-72 sample exhibits higher adsorption values over the whole 3M ionomer concentration range. In both cases, the 3M adsorption shows a good agreement to the Langmuir isotherm at low concentrations as has been reported previously for Nafion.²⁵⁶ The dotted lines in Figure 54 correspond to the fitted plots.

The adsorption parameters for both samples are summarized in Table 10. As expected from Figure 54, the Vulcan XC-72 sample exhibits a higher adsorption equilibrium constant, which would suggest a stronger binding between ionomer and support.

5.6 Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) Analysis

Given the limitations observed with the ¹⁹F NMR analysis, a different approach was used to study the ionomer adsorption on the carbon and carbon-supported Pt samples. ICP-OES was used to obtain the concentration of the equilibrium solutions, following the procedure described above.

Table 10. Adsorption parameters for the Langmuir isotherm for the Vulcan and 50% Pt/Vulcan samples obtained from the ^{19}F NMR analysis.

Adsorbent	Γ_{max} [$\text{g}_{3\text{Mlon}} \cdot \text{g}_s^{-1}$]	K_{eq}
Vulcan XC-72	$3.7 \cdot 10^{-2}$	9.46
50 % Pt/V72	$1.1 \cdot 10^{-2}$	7.67

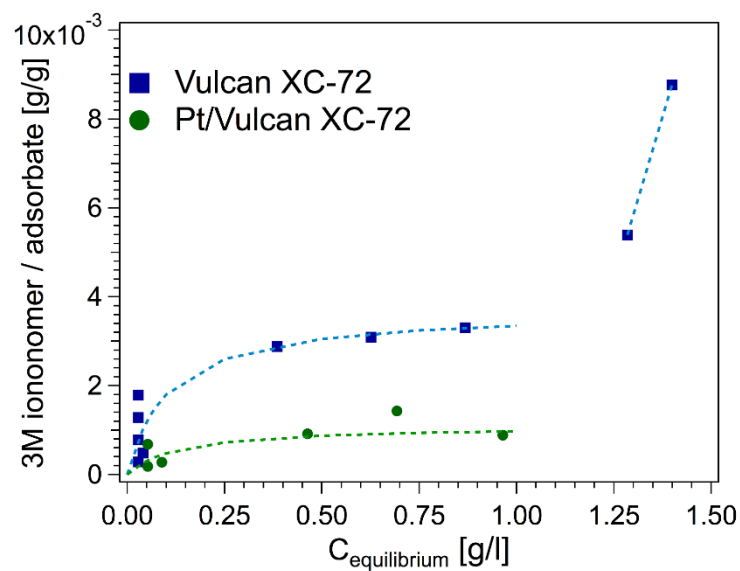


Figure 54. 3M Ionomer adsorption isotherms for Vulcan and Pt/Vulcan samples estimated from the ^{19}F NMR analysis showing the fitting to the Langmuir equation at low concentrations.

Figure 55 shows the adsorption behavior of the carbon samples obtained by this methodology. A similar behavior to that obtained through ^{19}F NMR analysis was observed. Similarly, Langmuir approach was used to obtain information on the adsorption behavior of the carbon samples. The estimated adsorption parameters for these samples are summarized in Table 11 along with the statistical results. The area-specific maximum surface coverage was obtained using the estimated BET surface area.

The highest equilibrium constant and area-specific maximum surface coverage correspond to the BP and V72 samples, respectively. These samples exhibited intermediate values of the I_D/I_G ratio. In contrast, both the AB and KJB samples, which exhibited the lowest and highest I_D/I_G ratios, respectively, showed lower Γ_{max} and K_{eq} values. This trend suggests that the carbon preferentially adsorbs on the amorphous/graphitic boundaries present in the turbostratic structure of carbon. These sites of the microcrystalline carbon domains are particularly known to be highly reactive, given their unsaturated electron density when compared to basal plane carbon. Studies have suggested preferential adsorption of Pt nanoparticles on these sites.^{5,252} The extent of such boundaries is minimal in the highly graphitic structures as illustrated in Figure 47.

The KJB structure, in contrast, corresponds to a turbostratic structure. In this case, the lower ionomer adsorption can be associated to the higher percentage of primary pores present in this type of carbon. In agreement with our previous

Table 11. Adsorption parameters for the Langmuir isotherm for the carbon samples obtained from the ICP-OES analysis

Adsorbent	Root mean square error	Parameters Estimate	Standard Error
Vulcan XC-72	$7.6 \cdot 10^{-3}$	$\Gamma_{max} = 0.05 g_{3M} \cdot g_S^{-1}$ $= 2.3 \cdot 10^{-4} g_{3M} \cdot m_s^{-2}$ $K_{eq} = 3.7$	$0.009 g_{3M} \cdot g_S^{-1}$ 1.8
BP2000 Carbon	$3.7 \cdot 10^{-2}$	$\Gamma_{max} = 0.27 g_{3M} \cdot g_S^{-1}$ $= 1.9 \cdot 10^{-4} g_{3M} \cdot m_s^{-2}$ $K_{eq} = 4.1$	$0.036 g_{3M} \cdot g_S^{-1}$ 1.4
Acetylene Black	$9.5 \cdot 10^{-3}$	$\Gamma_{max} = 0.15 g_{3M} \cdot g_S^{-1}$ $= 1.9 \cdot 10^{-3} g_{3M} \cdot m_s^{-2}$ $K_{eq} = 2.0$	$0.022 g_{3M} \cdot g_S^{-1}$ 0.7
KJB EC600JD	$9.0 \cdot 10^{-5}$	$\Gamma_{max} = 0.24 g_{3M} \cdot g_S^{-1}$ $= 1.6 \cdot 10^{-4} g_{3M} \cdot m_s^{-2}$ $K_{eq} = 1.5$	$0.014 g_{3M} \cdot g_S^{-1}$ 0.20

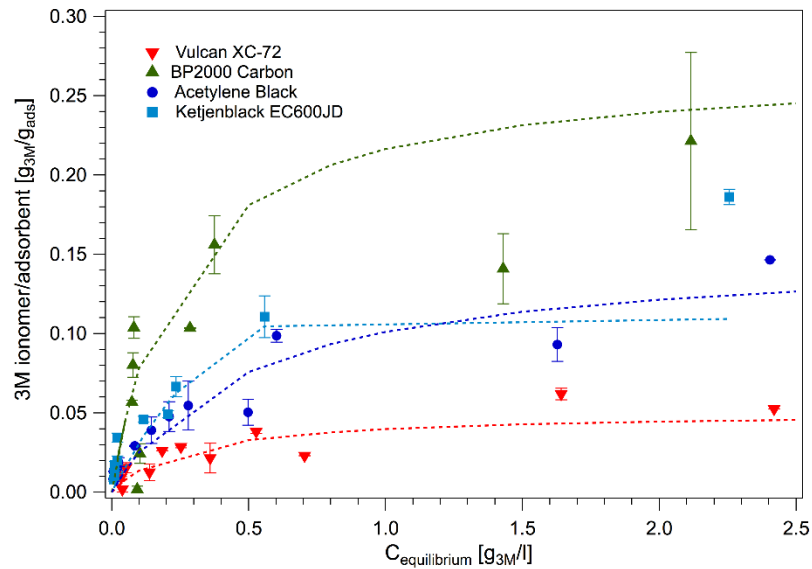


Figure 55. 3M Ionomer adsorption isotherms for the carbon samples estimated from the ICP-OES analysis showing the fitting to the Langmuir equation.

observations with free-standing electrodes and with results published in the literature, it has been concluded that the ionomer distributes on the surface of carbon agglomerates (i.e. within secondary pores) and is unable to access primary pores in the CL structure.^{5,30,165,166} This conclusion has been mainly based on gas sorption experiments where ionomer addition has exhibited a significant impact on the resulting secondary pore volume obtained. To explore this hypothesis the surface area value of each sample was corrected taking the secondary pore volume percentage into account. Considering the secondary pore volume percentages (obtained from BHJ calculation) for the V72 (99%), BP (88%) and KJB (73%), the corrected-area-specific maximum surface coverage are $2.28 \cdot 10^{-4}$, $2.21 \cdot 10^{-4}$ and $2.24 \cdot 10^{-4} \text{ g}_{3Mion} \cdot m_s^{-2}$, respectively.

These results represent further evidence that ionomer adsorption occurs mainly on the surface of the pores present within carbon agglomerates (i.e. secondary pores). This observation has several implications for the CL composition. First, this would imply that the support nanostructure and pore size distribution can control the ionomer distribution at a given CL composition. Turbostratic carbons with lower micropore volume can promote the development of a continuous ionomer network at lower ionomer contents than highly microporous material such as KJB. Furthermore, such distribution can imply that Pt nanoparticles located in the interior of micropores are inaccessible for protons and, therefore, electrochemically inactive. Reports by Soboleva et al. further support these arguments.³⁰ When

comparing proton conductivity and fuel cell performance for CLs prepared with V72 and KJB, the authors found that V72 exhibits a better performance (higher proton conductivity and current density values) than KJB at lower ionomer contents.

The mass-specific maximum coverage for each carbon sample allowed the calculation of the ionomer monolayer coverage. The values calculated were 5 wt.%, 21 wt. %, and 19 wt. % for the V72, BP, and KJB samples, respectively. Beyond these values, multilayer adsorption, and therefore, ionomer agglomeration can be expected to occur during CL formation. This result is particularly relevant given that the optimal ionomer content in the literature has been found to be approximately 30 wt. %.^{27,165} The higher ionomer coverage exhibited by the HSACs (BP and KJB) is consistent with our hypothesis that this type of carbon require mores ionomer to achieve a continuous proton transport network.

Figure 56 shows the adsorption behavior of V72 supported Pt particles. The adsorption isotherm for V72 has been included for comparison purposes. The trend observed with increasing Pt content agrees with that observed with the ¹⁹F NMR analysis. The estimated adsorption parameters for these samples are summarized in Table 12. The equilibrium constant shows a correlation with the Pt content on the V72 samples. This suggests that ionomer adsorption is promoted on the V72 surface. As the TEM micrographs showed, lower Pt content displays a larger area of the carbon exposed and available for adsorption. Furthermore, Pt nanoparticles can be hindering the preferential sites for ionomer adsorption.

Table 12. Adsorption parameters for the Langmuir isotherm for the V72 and Pt/V72 samples obtained from the ICP-OES analysis.

Adsorbent	Root mean square error	Parameters Estimate	Standard Error
Vulcan XC-72	$7.6 \cdot 10^{-3}$	$\Gamma_{max} = 0.05 g_{3M} \cdot g_S^{-1}$ $K_{eq} = 3.7$	$0.009 g_{3M} \cdot g_S^{-1}$ 1.8
30% Pt/V72	$6.2 \cdot 10^{-3}$	$\Gamma_{max} = 0.07 g_{3M} \cdot g_S^{-1}$ $K_{eq} = 2.0$	$0.008 g_{3M} \cdot g_S^{-1}$ 0.6
50% Pt/V72	$4.4 \cdot 10^{-3}$	$\Gamma_{max} = 0.04 g_{3M} \cdot g_S^{-1}$ $K_{eq} = 1.3$	$0.035 g_{3M} \cdot g_S^{-1}$ 1.7

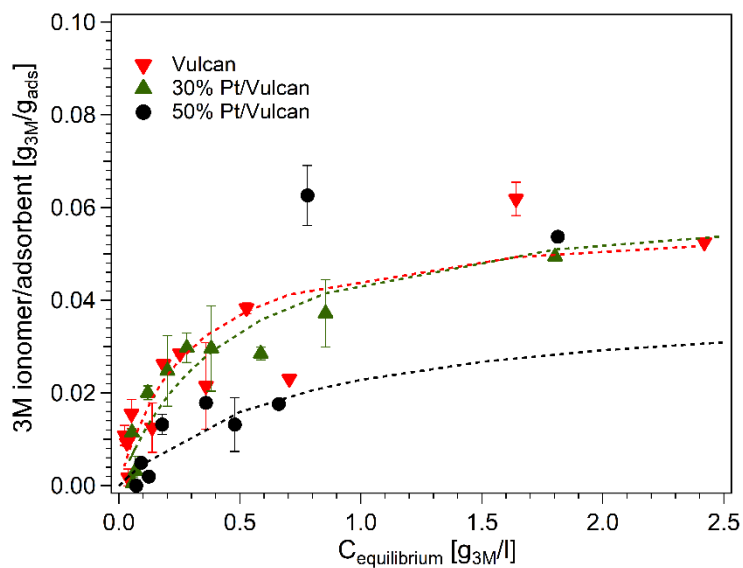


Figure 56. 3M Ionomer adsorption isotherms for the V72, and 30 and 50% Pt/V72 estimated from the ICP-OES analysis showing the fitting to the Langmuir approach.

5.7 Solid State Nuclear Magnetic Resonance

In an attempt to elucidate changes in the adsorbed ionomer structure that could reveal the nature of the substrate/ionomer interactions, SSNMR measurements were performed on the carbon-supported ionomer samples. Unfortunately, these measurements were limited to relatively high ionomer concentrations since the carbon affected instrument tuning. A representative ^{19}F SSNMR spectrum is shown in Figure 57, where the main peaks associated to the ionomer structure are shown.

Figure 58 shows the results obtained for ionomer adsorbed on the various carbon supports. No significant differences were observed in terms of chemical shift or peak broadening. This result can be explained by the high ionomer concentration used in this experiment. At this ionomer concentration, multilayer adsorption can occur leading to a bulk-like behavior. Consequently, these results are not conclusive.

5.8 Conclusions

The interactions between 3M 825 EW ionomer and different carbon supports were studied. Furthermore, the adsorption of ionomer on a series of Pt:C (0:100, 30:70, and 50:50) ratios using Vulcan XC-72 carbon as support were evaluated.

All samples showed a good agreement with the Langmuir isotherm at low concentrations. The highest equilibrium constant and area-specific maximum

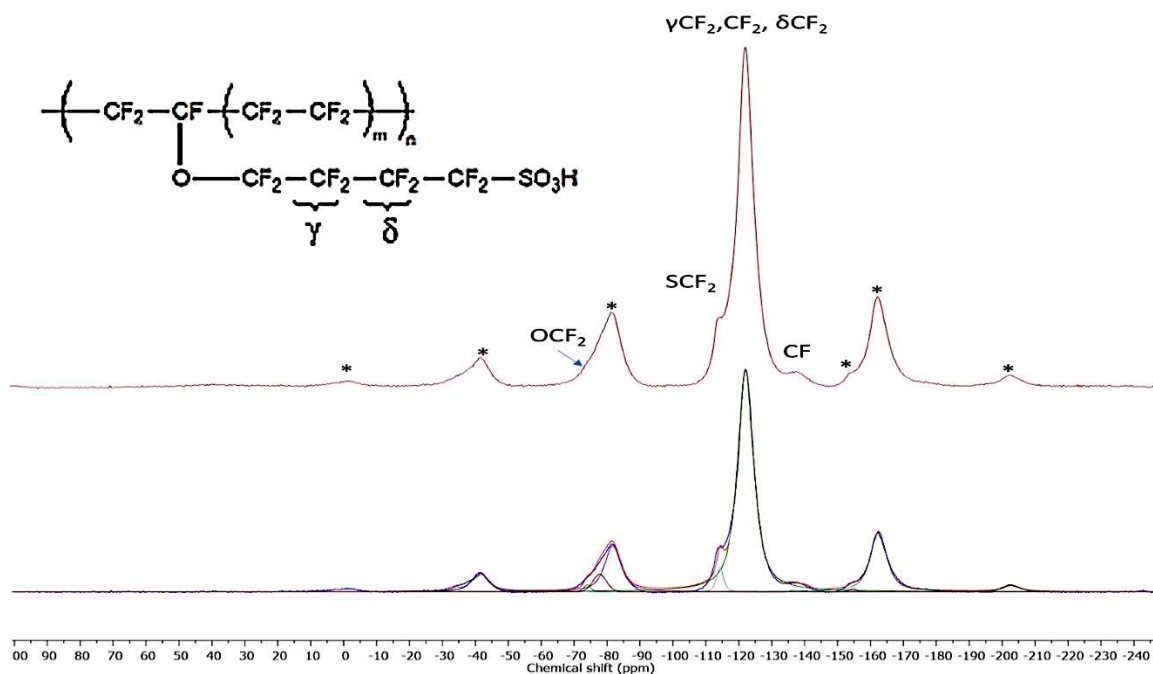


Figure 57. ^{19}F SSNMR spectrum of 3M 825 ionomer adsorbed on the carbon samples.

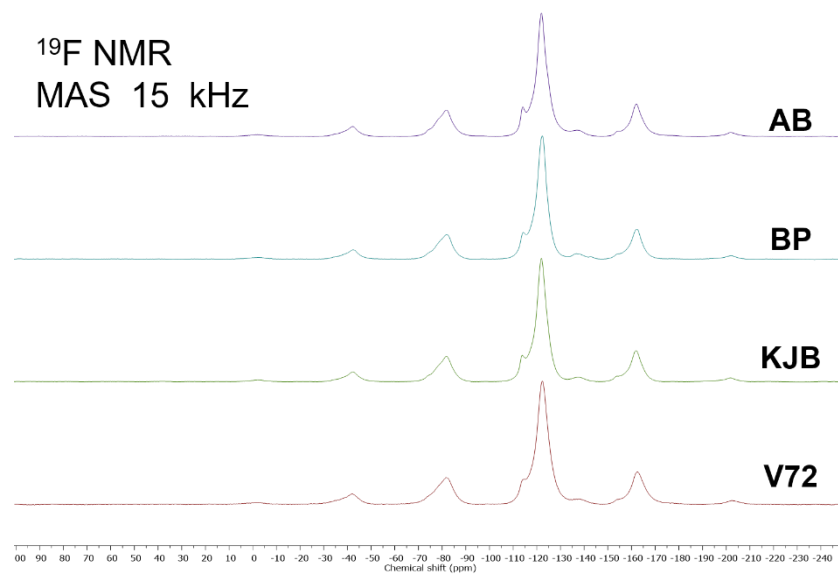


Figure 58. ^{19}F SSNMR spectra of 3M 825 ionomer adsorbed on the carbon supports.

surface coverage corresponds to the BP and V72 samples, respectively. These samples exhibited intermediate values of the I_D/I_G ratio, which suggests a turbostratic structure involving amorphous and graphitic domains. This trend suggests that the carbon preferentially adsorbs on the amorphous/graphitic boundaries present in the turbostratic structure of carbon. These boundaries are minimal in the highly graphitic structures

Furthermore, the use of the secondary pore surface area to correct the maximum surface coverage led to similar results for the V72, BP and KJB samples. This indicates that ionomer adsorption occurs mainly on the surface of the secondary pores as has been suggested by BET results previously. Furthermore, Pt nanoparticles can be hindering the preferential sites for ionomer adsorption.

The presence of Pt had a *negative* impact on the adsorption strength of 3M ionomer. The equilibrium constant shows a negative correlation with the Pt content on the V72 samples. This suggests that ionomer adsorption is primarily associated with the carbon surface.

Chapter 6

CONCLUSIONS

In this work, a thorough characterization and analysis of the PEMFC structure with different catalyst materials and compositions have been presented. Here the main conclusions are discussed in detail.

6.1 PGM-free Catalyst Layer

In Chapter 3, the characterization and fuel cell testing of a PGM-free cathode catalyst was performed. In PEMFCs the thickness, structure and morphology of the electrode CL are integral to cell performance. The effect of these parameter becomes particularly significant when the cathode catalyst is based on a non-precious metal due to the higher catalyst loadings required to compensate for the lower catalytic activity when compared to Pt based catalysts.

An iron (III) porphyrin framework material was synthesized and pyrolyzed and its catalytic activity towards the ORR was evaluated using RDE experiments and single cell testing. Single cell performance was evaluated as a function of the electrode catalyst loading (electrode thickness) and oxygen partial pressure. Emphasis was made in the electrode structure and its impact on the PEMFC performance. The conclusions obtained from this analysis regarding the synthesis process and the electrode structure impact will be discussed in the following sections.

6.1.1 Covalent-Heme-Framework-Based Catalyst Activation

The synthesized CHF-1 catalyst was evaluated through the RDE technique at different stages of the activation process. In particular, the pyrolysis step shown to be a key step in determining the catalytic activity of this material. Furthermore, the pyrolysis temperature exhibited a significant influence on the catalytic performance of the treated samples. Up to a 700°C pyrolysis temperature, an increase in onset potential along with a monotonous increase in limiting current density suggests that the formation of reaction sites and enhancement of the catalyst structure is promoted. The lower hydrogen peroxide yield observed at the best-performing temperature suggests that the 4-electron ORR pathway prevails at these conditions. However, a dramatic decrease in both parameters is evidenced beyond the 700°C pyrolysis temperature.

On the other hand, the acid treatment step did not exhibit a significant influence on the onset potential. Conversely, this step was determining for the limiting current density obtained with the treated sample. Further characterization with XRD and TEM revealed the presence of metallic iron after the acid treatment was performed. This is in agreement with recent studies, where the inability of this step to completely eliminate metallic iron nanoparticles has been established.⁹⁸ This was further confirmed by EDS and ICP-OES measurements where a significant iron percentage was obtained with the final sample. The improvement observed in terms of limiting current density was associated with the increase in porosity

observed with BET after the acid leaching. This effect can be ascribed to the removal of large iron particles that could block the catalyst pores.

6.1.2 Covalent-heme-framework-based PEMFC Electrode Evaluation

The H₂/O₂-Ar MEA performance was evaluated for different catalyst loadings and oxygen partial pressures to assess the mass transport influence on the performance of this material. The individual contributions to the PEMFC overall overpotential were evaluated. As expected, the ORR kinetic overpotential was the major contributor to the overall voltage loss. However, the mass transport contribution to the voltage loss became more prominent with small increases in the cathode catalyst loading. Through the analysis of the individual contributions to the voltage loss, a significant influence of the transport processes on the overall performance can be observed when the catalyst loading increases. A significant improvement of the overall cell performance was observed when the mass transport losses were ‘artificially’ reduced for the highest cathode catalyst loading. These results highlight the ‘trade-off’ between catalyst site density and electrode thickness: higher catalyst loading implies a higher number of active sites and, therefore, exhibits lower activation overpotential; however, this effect is counterbalanced by significantly higher mass transport contributions in the thicker electrode. This poses a limitation for the PGM-free catalyst loading and, ultimately for the PEMFC performance.

6.2 Pt-based-free-standing Electrodes

In Chapter 4, the structure and distribution of industrial-made electrodes were evaluated. In this study, a set of experimental techniques was adopted to characterize the fundamental properties of machine-prepared cathode CCLs formed by different Pt:C ratios, a highly graphitized carbon (EA carbon) and 3M ionomer (825EW) with a fixed I:C ratio. SEM, TEM and BET nitrogen adsorption were conducted to investigate the CCL microstructure including material dispersion and porosity. This analysis was performed on both the CL in an as-prepared condition and after being subjected to a standard PEMFC protocol.

6.2.1 *Electrode Structure and Pt particle size*

In all samples, the images showed preferential Pt deposition on the graphitic carbon structure defects, leading to a heterogeneous particle distribution throughout the CL. The highest Pt:C ratio exhibited a higher Pt particle size and degree of agglomeration. Although all samples exhibited a similar Pt particle size distribution behavior, significant differences were observed in terms of pore size distribution. Among the CL samples, the 70:30 Pt:C ratio presents a higher primary pore (small pores) volume, and the 30:70 Pt:C ratio sample exhibits the highest secondary pore (large pores) volume. Given that both the carbon support and the I:C ratio are fixed for the CL samples in this study, we attribute the changes in pore volume at the different Pt:C ratio to a variation in the ionomer distribution

throughout the CL pore structure. This behavior indicates that the ionomer has a higher affinity towards the carbon surface, which has been suggested by previous Nafion adsorption studies.^{199,200} Such affinity, along with the significant Pt particle agglomeration observed in the 70:30 Pt:C CL sample through TEM characterization can lead to higher ionomer agglomeration on the >20 nm mesopores, thus reducing the 'available' pore volume in this size range. In the 30:70 Pt:C ratio sample, in contrast, a lower degree of Pt particles agglomeration and a significantly lower particle size would allow a more homogeneous ionomer distribution.

6.2.2 *Transport Properties*

For these materials, the CL water uptake isotherms are similar in shape to that corresponding to the 3M bulk membrane and previous results from Nafion reports.^{184,202} However, a significant reduction in water uptake was observed with all the CL samples relative to the membrane, which is in agreement with previous observations in recast ionomer films.^{177,204–208} A decrease in water uptake in these thin ionomer films has been associated with an increase in the Young's modulus caused by polymer confinement²⁰⁵ or, as also likely, the effect of interaction of the ionomer with the support.

The 70:30 Pt:C ratio sample exhibits higher water uptake values than the 30:70 and 50:50 Pt:C ratio CL materials over the entire water vapor activity range, and it

also exhibits larger swelling at a lower RH. The higher uptake observed in the highest Pt:C ratio can be explained by two factors: (i) a higher primary pore (2-20 nm) volume, where capillary condensation of water can take place,^{5,30,167} and (ii) the larger ionomer agglomeration suggested by the BET characterization enables more bulk-like ionomer behavior. Overall, we note that the water uptake data suggest that higher Pt loading is associated with weaker interactions, leading to a suggestion that the ionomer-carbon interaction is a significant factor.

Conversely, the proton conductivity showed the opposite trend: the lowest Pt:C ratio exhibited the highest proton conductivity. This result coincides with the physicochemical characterization result: the higher secondary pore volume obtained with the 30:70 Pt:C ratio sample suggests lower ionomer accumulation in the pores and a more homogeneous ionomer distribution throughout the CL.

6.2.3 Fuel Cell Performance

A significant difference in PEMFC performance was observed particularly at low current density values (kinetic region). The 30:70 Pt:C ratio sample exhibited nearly a 100% increase in current density at 0.85 V over that of the 70:30 Pt:C ratio sample. Furthermore, the 30:70 Pt:C ratio cathode prevails over the whole current density range. This agrees with the characterization results: the 30:70 Pt:C ratio exhibited a lower degree of Pt agglomeration and Pt particle size and higher proton conductivity over the whole RH range.

6.3 3M Ionomer Adsorption

Further exploration of the effects observed with the free-standing samples motivated the evaluation of ionomer adsorption on different carbon and Pt/C structures. In this study, the interactions between 3M 825 EW ionomer and different carbon supports were studied. The adsorption of ionomer on a series of Pt:C (0:100, 30:70, and 50:50) ratios using Vulcan XC-72 Carbon as support was evaluated to further understand this interaction. The adsorption properties of water-dissolved 3M 825 EW ionomer on both the carbon supports and the series of Vulcan-supported platinum catalysts were studied with an NMR method adapted from the literature. This was found to be insensitive at lower ionomer concentrations and a new method was developed using ICP-OES for the quantitative analysis.

6.3.1 Carbon Support Effect

All samples showed a good adherence to the Langmuir isotherm at low concentrations. The highest equilibrium constant and area-specific maximum surface coverage correspond to the BP and V72 samples, respectively. These samples exhibited intermediate values of the I_D/I_G ratio, which suggests a turbostratic structure involving amorphous and graphitic domains. In contrast, both the AB and KJB samples, which exhibited the lowest and highest I_D/I_G ratios, respectively, showed lower Γ_{max} and K_{eq} values. This trend suggests that the

carbon preferentially adsorbs on the defects or boundaries present in the turbostratic structure of carbon. These defects are minimal in the highly graphitic structures.

6.3.2 *Platinum Particle Effect*

In agreement with our conclusions from the previous Chapter, the presence of Pt showed to have a negative impact in the adsorption strength of 3M ionomer. The ^{19}F NMR and the ICP-OES analysis techniques showed a similar trend. The equilibrium constant shows a negative correlation with the Pt content on the V72 samples. This suggests that ionomer adsorption is promoted on the V72 surface. As the TEM micrographs showed, lower Pt content displays a larger area of exposed carbon available for adsorption. From the results in Chapter 4 and Chapter 5, we conclude that the ionomer interaction with carbon-supported Pt catalysts is strongest with the carbon support.

REFERENCES

1. W. R. Grove, *The correlation of physical forces*, Sixth Ed., p. 1811-1896, Longsman, Green & Co., London, (1874).
2. J. Zhang, Ed., *PEM Fuel Cell Electrocatalysts and Catalyst Layers Fundamentals and Applications*, p. 1-1137, Springer London, (2008).
3. E. B. Yeager and A. J. Appleby, *Energy*, **11**, 137–152 (1986).
4. M. S. Wilson and S. Gottesfeld, *J. Appl. Electrochem.*, **22**, 1–7 (1992).
5. T. Soboleva, X. Zhao, K. Malek, Z. Xie, T. Navessin, and S. Holdcroft, *ACS Appl. Mater. Interfaces*, **2**, 375–384 (2010).
6. S. Sambandam and V. Ramani, *Phys. Chem. Chem. Phys.*, **12**, 6140–6149 (2010).
7. S. Sambandam, J. Parrondo, and V. Ramani, *Phys. Chem. Chem. Phys.*, **15**, 14994–5002 (2013).
8. X.-S. Wang, M. Chrzanowski, D. Yuan, B. S. Sweeting, and S. Ma, *Chem. Mater.*, **26**, 1639–1644 (2014).
9. J. Zagal, F. Bedioui, and J. P. Dodelet, Eds., *N4-macrocyclic metal complexes*, (2007).
10. G. Wu, Z. Chen, K. Artyushkova, F. H. Garzon, and P. Zelenay, *Ecs Trans.*, **16**, 159–170 (2008).
11. A. B. Papandrew, S. S. John, R. A. Elgammal, D. L. Wilson, R. W. Atkinson, J.

- S. Lawton, T. M. Arruda, and T. A. Zawodzinski, *J. Electrochem. Soc.*, **163**, F464–F469 (2016).
12. G. a. Goenaga, A. Belapure, C. Zhang, A. B. Papandrew, S. Foister, and T. A. Zawodzinski, *ECS ...*, **41**, 1193–1205 (2011).
13. A. Pebler, *J. Electrochem. Soc.*, **133**, 9 (1986).
14. X. Cheng, B. Yi, M. Han, J. Zhang, Y. Qiao, and J. Yu, *J. Power Sources*, **79**, 75–81 (1999).
15. J. Aragane, *J. Electrochem. Soc.*, **135**, 844 (1988).
16. K. L. More, R. Borup, and K. S. Reeves, *ECS Trans.*, **1**, 717–733 (2006).
17. D. A. Blom, J. R. Dunlap, T. A. Nolan, and L. F. Allard, *J. Electrochem. Soc.*, **150**, A414 (2003).
18. D. C. Montgomery, *Applied Statistics and Probability for Engineers Third Edition*, p. 455, (2003).
19. B. G. Tabachnick and L. Fidell, *Using multivariate statistics* L. S. Fidell, Editor, 5th Ed., Allyn & Bacon/Pearson Education, Boston, MA, (2007).
20. A. L. Patterson, *Phys. Rev.*, **56**, 978–982 (1939).
21. G. Fagerlund, *Matériaux Constr.*, **6**, 239–245 (1973).
22. S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309–319 (1938).

23. Quantachrome Instruments, *Gas Sorption System Operating Manual*, p. 365-366, Boynton Beach, FL, (2013).
24. E. P. Barrett, L. G. L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373–380 (1951).
25. L. D. Gelb and K. E. Gubbins, *Langmuir*, **14**, 2097–2111 (1998).
26. E. A. Ticianelli, C. R. Derouin, and S. Srinivasan, *J. Electroanal. Chem. Interfacial Electrochem.*, **251**, 275–295 (1988).
27. N. Zamel, *J. Power Sources*, **309**, 141–159 (2016).
28. T. Biegler, D. A. J. Rand, and R. Woods, *J. Electroanal. Chem. Interfacial Electrochem.*, **29**, 269–277 (1971).
29. X. Z. Yuan, C. Song, H. Wang, and Z. J., *Electrochemical Impedance Spectroscopy in PEM Fuel Cells: Fundamentals and Applications*, p. 1689-1699, Springer, (2010).
30. T. Soboleva, K. Malek, Z. Xie, T. Navessin, and S. Holdcroft, *ACS Appl. Mater. Interfaces*, **3**, 1827–1837 (2011).
31. M. Eikerling and A. . Kornyshev, *J. Electroanal. Chem.*, **475**, 107–123 (1999).
32. G. Leofanti, M. Padovan, G. Tozzola, and B. Venturelli, *Catal. Today*, **41**, 207–219 (1998).
33. K. Kaneko, *Determination of pore size and pore size distribution. 1. Adsorbents*

and catalysts, (1994), p. 59–89.

34. H. A. Gasteiger, S. S. Kocha, B. Sompalli, and F. T. Wagner, *Appl. Catal. B Environ.*, **56**, 9–35 (2005).

35. U.S. Department of Energy, *Multi-Year Research, Development, and Demonstration Plan: Fuel Cells*, (2016).

36. I. Matanovic, K. Artyushkova, and P. Atanassov, *Curr. Opin. Electrochem.* (2018).

37. C. H. Choi, W. S. Choi, O. Kasian, A. K. Mechler, M. T. Sougrati, S. Brüller, K. Strickland, Q. Jia, S. Mukerjee, K. J. J. Mayrhofer, and F. Jaouen, *Angew. Chemie - Int. Ed.*, **56**, 8809–8812 (2017).

38. Q. Jia, N. Ramaswamy, U. Tylus, K. Strickland, J. Li, A. Serov, K. Artyushkova, P. Atanassov, J. Anibal, C. Gumezi, S. C. Barton, M. T. Sougrati, F. Jaouen, B. Halevi, and S. Mukerjee, *Nano Energy* (2016).

39. E. F. Holby, G. Wu, P. Zelenay, and C. D. Taylor, *J. Phys. Chem. C*, **118**, 14388–14393 (2014).

40. K. Artyushkova, A. Serov, S. Rojas-Carbonell, and P. Atanassov, *J. Phys. Chem. C*, **119**, 25917–25928 (2015).

41. S. Kattel, P. Atanassov, and B. Kiefer, *Phys. Chem. Chem. Phys.*, **16**, 13800 (2014).

42. T. S. Olson, S. Pylypenko, J. E. Fulghum, and P. Atanassov, *J. Electrochem. Soc.*, **157**, B54 (2010).
43. A. Serov, U. Tylus, K. Artyushkova, S. Mukerjee, and P. Atanassov, *Appl. Catal. B Environ.*, **150–151**, 179–186 (2014).
44. G. Wu, K. L. More, C. M. Johnston, and P. Zelenay, *Science (80-.)*, **332**, 443–447 (2011).
45. H. T. Chung, C. M. Johnston, K. Artyushkova, M. Ferrandon, D. J. Myers, and P. Zelenay, *Electrochem. commun.*, **12**, 1792–1795 (2010).
46. U. I. Kramm, I. Herrmann-Geppert, P. Bogdanoff, and S. Fiechter, *J. Phys. Chem. C*, 23417–23427 (2011).
47. S.-T. Chang, C.-H. Wang, H.-Y. Du, H.-C. Hsu, C.-M. Kang, C.-C. Chen, J. C. S. Wu, S.-C. Yen, W.-F. Huang, L.-C. Chen, M. C. Lin, and K.-H. Chen, *Energy Environ. Sci.*, **5**, 5305–5314 (2012).
48. E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Tian, J. Herranz, and J.-P. Dodelet, *Nat. Commun.*, **2**, 416 (2011).
49. M. Lefèvre, E. Proietti, F. Jaouen, and J.-P. Dodelet, *Science*, **324**, 71–4 (2009).
50. M. Kiani, J. Zhang, Y. Luo, C. Jiang, J. Fan, G. Wang, J. Chen, and R. Wang, *J. Energy Chem.* (2018).

51. H. Zhang, H. Osgood, X. Xie, Y. Shao, and G. Wu, *Nano Energy*, **31**, 331–350 (2017).
52. R. Jasinski, *Nature*, **201**, 1212–1213 (1964).
53. H. Jahnke, M. Schönborn, and G. Zimmermann, in *Physical and Chemical Applications of Dyestuffs*,, p. 133–181 (1974).
54. V. S. Bagotzky, M. R. Tarasevich, K. A. Radyushkina, O. A. Levina, and S. I. Andrusyova, *J. Power Sources*, **2**, 233–240 (1978).
55. E. B. Yeager, *Electrochim. Acta*, **29**, 1527–1537 (1984).
56. D. Scherson, C. Fterro, and W. Reserve, *Electrochim. Acta*, **28**, 1205–1209 (1983).
57. J. A. R. Van Veen, H. A. Colijn, and J. F. Van Baar, *Electrochim. Acta*, **33**, 801–804 (1988).
58. J. A. R. Van Veen, J. F. Van Baar, and K. J. Kroese, *J. Chem. Soc. Faraday Trans. I*, **77**, 2827–2843 (1981).
59. R. W. Joyner, J. A. R. Van Veen, and W. M. H. Sachtler, *J. Chem. Soc. Faraday Trans. 1*, **78**, 1021–1028 (1982).
60. Y. Liu, X. Yue, K. Li, J. Qiao, D. P. Wilkinson, and J. Zhang, *Coord. Chem. Rev.*, **315**, 153–177 (2016).
61. S. Gupta, D. A. Tryk, I. Bae, W. Aldred, and E. B. Yeager, *J. Appl.*

Electrochem., **19**, 19–27 (1989).

62. D. Ohms, S. Herzog, R. Franke, V. Neumann, K. Wiesener, S. Gamburgcev, A. Kaisheva, and I. Iliev, *J. Power Sources*, **38**, 327–334 (1992).

63. S. Ye and A. K. Vijh, *Electrochem. commun.*, **5**, 272–275 (2003).

64. G. Liu, X. Li, P. Ganesan, and B. N. Popov, *Appl. Catal. B Environ.*, **93**, 156–165 (2009).

65. A. Jindal, D. K. Gautam, and S. Basu, *J. Electroanal. Chem.*, **775**, 198–204 (2016).

66. G. Lalande, R. Côté, D. Guay, J.-P. Dodelet, L. T. Weng, and P. Bertrand, *Electrochim. Acta*, **42**, 1379–1388 (1997).

67. C. Fabjan, G. Frithum, and H. Hartl, *Berichte der Bunsengesellschaft für Phys. Chemie*, **94**, 937–941 (1990).

68. W. Seeliger and A. Hamnett, *Electrochim. Acta*, **37**, 763–765 (1992).

69. A. L. Bouwkamp-Wijnoltz, W. Visscher, J. A. R. Van Veen, and S. C. Tang, *Electrochim. Acta*, **45**, 379–386 (1999).

70. R. Bashyam and P. Zelenay, *Nature*, **443**, 63–6 (2006).

71. M. Yuasa, A. Yamaguchi, H. Itsuki, and K. Tanaka, *Chem.Mater.*, **17**, 4278–4281 (2005).

72. W. Martínez Millán, T. Toledano Thompson, L. G. Arriaga, and M. A. Smit, *Int.*

- J. Hydrogen Energy*, **34**, 694–702 (2009).
73. W. Martínez Millán and M. A. Smit, *J. Appl. Polym. Sci.*, **112**, 2959–2967 (2009).
74. K. Lee, L. Zhang, H. Lui, R. Hui, Z. Shi, and J. Zhang, *Electrochim. Acta*, **54**, 4704–4711 (2009).
75. T. E. Wood, Z. Tan, A. K. Schmoeckel, D. O'Neill, and R. T. Atanasoski, *J. Power Sources*, **178**, 510–516 (2008).
76. G. Wu, K. Artyushkova, M. Ferrandon, A. J. Kropf, D. J. Myers, and P. Zelenay, *ECS Trans.*, **25**, 1299–1311 (2009).
77. G. Wu, M. a Nelson, N. H. Mack, S. Ma, P. Sekhar, F. H. Garzon, and P. Zelenay, *Chem. Commun. (Camb.)*, **46**, 7489–91 (2010).
78. P. Zamani, D. Higgins, F. Hassan, G. Jiang, J. Wu, S. Abureden, and Z. Chen, *Electrochim. Acta*, **139**, 111–116 (2014).
79. P. Zamani, D. C. Higgins, F. M. Hassan, X. Fu, J.-Y. Choi, M. A. Hoque, G. Jiang, and Z. Chen, *Nano Energy*, **26**, 267–275 (2016).
80. G. Liu, X. Li, P. Ganesan, and B. N. Popov, *Electrochim. Acta*, **55**, 2853–2858 (2010).
81. X. Li, G. Liu, and B. N. Popov, *J. Power Sources*, **195**, 6373–6378 (2010).
82. G. A. Goenaga, S. Ma, S. Yuan, and D. Liu, *ECS Trans.*, **33**, 579–586 (2010).

83. S. Ma, G. A. Goenaga, A. V. Call, and D. J. D.-J. Liu, *Chemistry*, **17**, 2063–7 (2011).
84. A. Sarapuu, L. Samolberg, K. Kreek, M. Koel, L. Matisen, and K. Tammeveski, *J. Electroanal. Chem.*, **746**, 9–17 (2015).
85. J. Anibal, H. G. Romero, N. D. Leonard, C. Gumecci, B. Halevi, and S. Calabrese Barton, *Appl. Catal. B Environ.*, **198**, 32–37 (2016).
86. A. Morozan and F. Jaouen, *Energy Environ. Sci.*, **5**, 9269 (2012).
87. L. Yang, N. Larouche, R. R. Chenitz, G. Zhang, M. Lefèvre, and J.-P. Dodelet, *Electrochim. Acta*, **159**, 184–197 (2015).
88. F. Jaouen, J. Herranz, M. Lefèvre, J.-P. Dodelet, U. I. Kramm, I. Herrmann, P. Bogdanoff, J. Maruyama, T. Nagaoka, A. Garsuch, J. R. Dahn, T. Olson, S. Pylypenko, P. Atanassov, and E. A. Ustinov, *ACS Appl. Mater. Interfaces*, **1**, 1623–39 (2009).
89. H. J. Mackintosh, P. M. Budd, and N. B. McKeown, *J. Mater. Chem.*, **18**, 573 (2008).
90. A. I. Cooper, *Adv. Mater.*, **21**, 1291–1295 (2009).
91. A. M. Shultz, O. K. Farha, J. T. Hupp, and S. T. Nguyen, *Chem. Sci.*, **2**, 686 (2011).
92. Y. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, **41**, 2083–94 (2012).

93. D. Banham, S. Ye, K. Pei, J. Ozaki, T. Kishimoto, and Y. Imashiro, *J. Power Sources*, **285**, 334–348 (2015).
94. J.-Y. Choi, L. Yang, T. Kishimoto, X. Fu, S. Ye, Z. Chen, and D. Banham, *Energy Environ. Sci.*, **10**, 296–305 (2017).
95. D. Banham, T. Kishimoto, Y. Zhou, T. Sato, K. Bai, J. Ozaki, Y. Imashiro, and S. Ye, *Sci. Adv.*, **4**, eaar7180 (2018).
96. M. Ferrandon, X. Wang, A. J. Kropf, D. J. Myers, G. Wu, C. M. Johnston, and P. Zelenay, *Electrochim. Acta*, **110**, 282–291 (2013).
97. D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun, and X. Bao, *Angew. Chemie - Int. Ed.*, **52**, 371–375 (2013).
98. C. H. Choi, C. Baldizzone, G. Polymeros, E. Pizzutilo, O. Kasian, A. K. Schuppert, N. Ranjbar Sahraie, M. T. Sougrati, K. J. J. Mayrhofer, and F. Jaouen, *ACS Catal.*, **6**, 3136–3146 (2016).
99. J. A. Varnell, E. C. M. Tse, C. E. Schulz, T. T. Fister, R. T. Haasch, J. Timoshenko, A. I. Frenkel, and A. A. Gewirth, *Nat. Commun.*, **7** (2016).
100. C. H. Choi, C. Baldizzone, J. P. Grote, A. K. Schuppert, F. Jaouen, and K. J. J. Mayrhofer, *Angew. Chemie - Int. Ed.*, **54**, 12753–12757 (2015).
101. V. Goellner, V. Armel, A. Zitolo, E. Fonda, and F. Jaouen, *J. Electrochem. Soc.*, **162**, H403–H414 (2015).

102. J. Herranz, F. Jaouen, M. Lefèvre, U. I. Kramm, E. Proietti, J.-P. Dodelet, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, P. Bertrand, T. M. Arruda, and S. Mukerjee, *J. Phys. Chem. C*, **115**, 16087–16097 (2011).
103. G. Zhang, R. Chenitz, M. Lefèvre, S. Sun, and J.-P. Dodelet, *Nano Energy*, **29**, 111–125 (2016).
104. B. Wang, *J. Power Sources*, **152**, 1–15 (2005).
105. S. Baranton, C. Coutanceau, C. Roux, F. Hahn, and J. M. Léger, *J. Electroanal. Chem.*, **577**, 223–234 (2005).
106. H. Meier, U. Tschirwitz, E. Zimmerhackl, W. Albrecht, and G. Zeitler, *J. Phys. Chem.*, **81**, 712–718 (1977).
107. A. Biloul, P. Gouérec, M. Savy, G. Scarbeck, S. Besse, and J. Riga, *J. Appl. Electrochem.*, **26**, 1139–1146 (1996).
108. K. Strickland, E. Miner, Q. Jia, U. Tylus, N. Ramaswamy, W. Liang, M. T. Sougrati, F. Jaouen, and S. Mukerjee, *Nat. Commun.*, **6** (2015).
109. G. Lalande, R. Côté, G. Tamizhmani, D. Guay, J.-P. Dodelet, L. Dignard-Bailey, L. T. Weng, and P. Bertrand, *Electrochim. Acta*, **40**, 2635–2646 (1995).
110. H. Alt, H. Binder, and G. Sandstede, *J. Catal.*, **28**, 8–19 (1973).
111. H. Schulenburg, S. Stankov, V. Schu, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, V. Schünemann, J. Radnik, I. Dorbandt, S. Fiechter, P.

- Bogdanoff, and H. Tributsch, *J. Phys. Chem. B*, **107**, 9034–9041 (2003).
112. L. Gubler, S. M. Dockheer, and W. H. Koppenol, *J. Electrochem. Soc.*, **158**, B755 (2011).
113. C. Walling, *Acc. Chem. Res.*, **8**, 125–131 (1975).
114. F. D. Coms, in *ECS Transactions*,, vol. 16, p. 235–255 (2008).
115. D. E. Curtin, R. D. Lousenberg, T. J. Henry, P. C. Tangeman, and M. E. Tisack, *J. Power Sources*, **131**, 41–48 (2004).
116. C. Zhou, M. A. Guerra, Z. M. Qiu, T. A. Zawodzinski, and D. A. Schiraldi, *Macromolecules*, **40**, 8695–8707 (2007).
117. G. Liu, X. Li, J.-W. Lee, and B. N. Popov, *Catal. Sci. Technol.*, **1**, 207 (2011).
118. G. Liu, X. Li, and B. N. Popov, in *ECS Transactions*,, p. 1251–1259 (2009).
119. J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, and K. M. Thomas, *Carbon N. Y.*, **33**, 1641–1653 (1995).
120. M. Lefèvre, J.-P. Dodelet, and P. Bertrand, *J. Phys. Chem. B*, **106**, 8705–8713 (2002).
121. F. Jaouen, M. Lefèvre, J.-P. Dodelet, and M. Cai, *J. Phys. Chem. B*, **110**, 5553–5558 (2006).
122. M. Ferrandon, A. J. Kropf, D. J. Myers, K. Artyushkova, U. Kramm, P. Bogdanoff, G. Wu, C. M. Johnston, and P. Zelenay, *J. Phys. Chem. C* (2012).

123. M. Shao, Q. Chang, J.-P. Dodelet, and R. Chenitz, *Chem. Rev.*, **116**, 3594–3657 (2016).
124. G. Denuault, M. Sosna, and K. Williams, in *Handbook of Electrochemistry*, C. Zoski, Editor, p. 431–469 (2006).
125. D. Banham, T. Kishimoto, T. Sato, Y. Kobayashi, K. Narizuka, J. Ozaki, Y. Zhou, E. Marquez, K. Bai, and S. Ye, *J. Power Sources*, **344**, 39–45 (2017).
126. T. S. Olson, K. Chapman, and P. Atanassov, *J. Power Sources*, **183**, 557–563 (2008).
127. S. Stariha, K. Artyushkova, M. J. Workman, A. Serov, S. Mckinney, B. Halevi, and P. Atanassov, *J. Power Sources*, **326**, 43–49 (2016).
128. S. Stariha, K. Artyushkova, A. Serov, and P. Atanassov, in *International Journal of Hydrogen Energy*,, vol. 40, p. 14676–14682 (2015).
129. A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M. T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, *Nano Energy*, **16**, 293–300 (2015).
130. S. L. Gojkovic, S. Gupta, and R. F. Savinell, *J. Electrochem. Soc.*, **145**, 3493 (1998).
131. M. Ciureanu and R. Roberge, *J. Phys. Chem. B*, **105**, 3531–3539 (2001).
132. S. Cruz-Manzo and R. Chen, *J. Electroanal. Chem.*, **694**, 45–55 (2013).

133. C. Boyer, S. Gamburgzev, O. Velez, S. Srinivasan, and A. J. Appleby, *Electrochim. Acta*, **43**, 3703–3709 (1998).
134. E. L. Gyenge, *J. Power Sources*, **152**, 105–121 (2005).
135. M. Uchida, Y. Aoyama, N. Eda, and A. Ohta, *J. Electrochem. Soc.*, **142**, 4143–4149 (1995).
136. I. D. Raistrick, (1989).
137. M. S. Wilson, J. A. Valerio, and S. Gottesfeld, *Electrochim. Acta*, **40**, 355–363 (1995).
138. M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, **139**, L28–L30 (1992).
139. W. Dai, H. Wang, X.-Z. Yuan, J. J. Martin, D. Yang, J. Qiao, and J. Ma, *Int. J. Hydrogen Energy*, **34**, 9461–9478 (2009).
140. K. Jiao and X. Li, *Prog. Energy Combust. Sci.*, **37**, 221–291 (2011).
141. M. K. Debe, *Handb. fuel cells*, 1–14 (2010).
142. M. K. Debe, *J. Electrochem. Soc.*, **160**, F522–F534 (2013).
143. M. K. Debe, A. A. Schmoeckel, S. Hendricks, G. D. Vernstrom, G. Haugen, R. T. Atanasoski, and G. M. H. and R. T. A. M. K. Debe, A. K. Schmoeckel, S. M. Hendricks, G. D. Vernstrom, *ECS Trans.*, **1**, 51–66 (2006).
144. M. K. Debe, A. K. Schmoeckel, G. D. Vernstrom, and R. T. Atanasoski, *J. Power Sources*, **161**, 1002–1011 (2006).

145. M. K. Debe, S. J. Hamrock, and R. T. Atanasoski, 301–308 (2005).
146. D. Gruber, N. Ponath, J. Müller, and F. Lindstaedt, *J. Power Sources*, **150**, 67–72 (2005).
147. J.-H. Wee, K.-Y. Lee, and S. H. Kim, *J. Power Sources*, **165**, 667–677 (2007).
148. R. O'hayre, S. J. Lee, S. W. Cha, and F. B. Prinz, *J. Power Sources*, **109**, 483–493 (2002).
149. F. J. Perez-Alonso, D. N. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I. E. L. Stephens, J. H. Nielsen, and I. Chorkendorff, *Angew. Chemie - Int. Ed.*, **51**, 4641–4643 (2012).
150. K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. R. Stamenkovic, M. Arenz, and N. M. Markovic, *Electrochim. Acta*, **53**, 3181–3188 (2008).
151. E. Antolini, *Appl. Catal. B Environ.*, **181**, 298–313 (2016).
152. C. Wang, H. Daimon, T. Onodera, T. Koda, and S. Sun, *Angew. Chemie - Int. Ed.*, **47**, 3588–3591 (2008).
153. Z. Chen, J.-P. Dodelet, and J. Zhang, *Non-Noble Metal Fuel Cell Catalysts*, p. 1-428, (2014).
154. N. M. Marković, R. R. Adzic, B. D. Cahan, and E. B. Yeager, *J. Electroanal. Chem.*, **377**, 249–259 (1994).
155. K. Kinoshita, *J. Electrochem. Soc.*, **137**, 845 (1990).

156. S. Mukerjee and J. McBreen, *J. Electroanal. Chem.*, **448**, 163–171 (1998).
157. Y. Takasu, N. Ohashi, X. G. Zhang, Y. Murakami, H. Minagawa, S. Sato, and K. Yahikozawa, *Electrochim. Acta*, **41**, 2595–2600 (1996).
158. C. Kuhrt and M. Harsdorff, *Surf. Sci.*, **245**, 173–179 (1991).
159. G. K. Wertheim, S. B. DiCenzo, and D. N. E. Buchanan, *Phys. Rev. B*, **33**, 5384–5390 (1986).
160. M. D. Maciá, J. M. Campiña, E. Herrero, and J. M. Feliu, *J. Electroanal. Chem.*, **564**, 141–150 (2004).
161. A. Kuzume, E. Herrero, and J. M. Feliu, *J. Electroanal. Chem.*, **599**, 333–343 (2007).
162. A. N. Frumkin and O. A. Petrii, *Electrochim. Acta*, **20**, 347–359 (1975).
163. K. J. J. Mayrhofer, B. B. Blizanac, M. Arenz, V. R. Stamenkovic, P. N. Ross, and N. M. Markovic, *J. Phys. Chem. B*, **109**, 14433–14440 (2005).
164. K. Kinoshita, (1988).
165. S. Holdcroft, *Chem. Mater.*, **26**, 381–393 (2014).
166. M. El Hannach, T. Soboleva, K. Malek, A. A. Franco, M. Prat, J. Pauchet, and S. Holdcroft, *J. Power Sources*, **247**, 322–326 (2014).
167. M. Eikerling, *J. Electrochem. Soc.*, **153**, E58 (2006).

168. Y.-C. Park, H. Tokiwa, K. Kakinuma, M. Watanabe, and M. Uchida, *J. Power Sources*, **315**, 179–191 (2016).
169. R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. J. Myers, M. Wilson, F. H. Garzon, D. Wood, P. Zelenay, K. L. More, K. Stroh, T. A. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, et al., *Chem. Rev.*, **107**, 3904–3951 (2007).
170. C. Y. Ahn, J. Y. Cheon, S. H. Joo, and J. Kim, *J. Power Sources*, **222**, 477–482 (2013).
171. X. Zhao, W. Li, Y. Fu, and A. Manthiram, *Int. J. Hydrogen Energy*, **37**, 9845–9852 (2012).
172. E. Antolini, L. Giorgi, A. Pozio, and E. Passalacqua, *J. Power Sources*, **77**, 136–142 (1999).
173. E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, and L. Giorgi, *Electrochim. Acta*, **46**, 799–805 (2001).
174. J. Xie, F. Xu, D. L. Wood, K. L. More, T. A. Zawodzinski, and W. H. Smith, *Electrochim. Acta*, **55**, 7404–7412 (2010).
175. Y. Liu, C. Ji, W. Gu, J. Jorne, and H. a. Gasteiger, *J. Electrochem. Soc.*, **158**, B614 (2011).
176. K. A. Mauritz and R. B. Moore, *Chem. Rev.*, **104**, 4535–4586 (2004).

177. D. K. Paul, A. Fraser, and K. Karan, *Electrochem. commun.*, **13**, 774–777 (2011).
178. Z. Siroma, R. Kakitsubo, N. Fujiwara, T. Ioroi, S. Yamazaki, and K. Yasuda, *J. Power Sources*, **189**, 994–998 (2009).
179. R. Subbaraman, D. Strmcnik, V. R. Stamenkovic, and N. M. Markovic, *J. Phys. Chem. C*, **114**, 8414–8422 (2010).
180. K. Kodama, R. Jinnouchi, T. Suzuki, H. Murata, T. Hatanaka, and Y. Morimoto, *Electrochem. commun.*, **36**, 26–28 (2013).
181. A. Kusoglu and A. Z. Weber, *Chem. Rev.*, **117**, 987–1104 (2017).
182. N. Agmon, *Chem. Phys. Lett.*, **244**, 456–462 (1995).
183. T. A. Zawodzinski, M. Neeman, L. O. Sillerud, and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040–6044 (1991).
184. T. A. Zawodzinski, C. R. Derouin, S. Radzinski, R. J. Sherman, V. T. Smith, T. E. Springer, and S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 1041–1047 (1993).
185. A. P. Saab, F. H. Garzon, and T. A. Zawodzinski, *J. Electrochem. Soc.*, **149**, A1541 (2002).
186. Y. Liu, M. W. Murphy, D. R. Baker, W. Gu, C. Ji, J. Jorne, and H. a. Gasteiger, *J. Electrochem. Soc.*, **156**, B970 (2009).
187. J. Liu and M. Eikerling, *Electrochim. Acta*, **53**, 4435–4446 (2008).

188. C.-N. Sun and T. A. Zawodzinski, *ECS Electrochem. Lett.*, **11**, 36–39 (2012).
189. A. Kongkanand, *J. Phys. Chem. C*, **115**, 11318–11325 (2011).
190. D. R. P. Morris, S. P. Liu, D. Villegas Gonzalez, and J. T. Gostick, *ACS Appl. Mater. Interfaces*, **6**, 18609–18618 (2014).
191. T. Shimura, K. Miyatake, and M. Watanabe, *Eur. Polym. J.*, **44**, 4054–4062 (2008).
192. M. Wissler, *J. Power Sources*, **156**, 142–150 (2006).
193. L. Castanheira, L. Dubau, M. Mermoux, G. Berthome, N. Caque, E. Rossinot, M. Chatenet, and F. Maillard, *ACS Catal.*, **4**, 2258–2267 (2014).
194. L. Castanheira, W. O. Silva, F. H. Lima, A. Crisci, L. Dubau, and F. Maillard, *ACS Catal.*, **5**, 2184–2194 (2015).
195. W. Trochim and J. P. Donnelly, *Research Methods Knowledge Base*, p. 361, (2006).
196. E. Theodorsson-Norheim, *Comput. Methods Programs Biomed.*, **23**, 57–62 (1986).
197. K. Sasaki, M. Shao, and R. R. Adzic, in *Polymer Electrolyte Fuel Cell Durability*, F. N. Büchi, M. Inaba, and T. J. Schmidt, Editors, p. 7–27, Springer New York, New York, NY (2009).
198. H. Ishikawa, Y. Sugawara, G. Inoue, and M. Kawase, *J. Power Sources*, **374**,

196–204 (2018).

199. S. MA, Q. CHEN, F. JOGENSEN, P. STEIN, and E. SKOU, *Solid State Ionics*, **178**, 1568–1575 (2007).

200. S. M. Andersen, *Appl. Catal. B Environ.*, **181**, 146–155 (2016).

201. G. Sasikumar, J. W. Ihm, and H. Ryu, *J. Power Sources*, **132**, 11–17 (2004).

202. A. Kusoglu, A. Kwong, K. T. Clark, H. P. Gunterman, and A. Z. Weber, *J. Electrochem. Soc.*, **159**, 530–535 (2012).

203. H. Iden, K. Sato, A. Ohma, and K. Shinohara, *J. Electrochem. Soc.*, **158**, B987 (2011).

204. K. A. Page, J. W. Shin, S. A. Eastman, B. W. Rowe, S. Kim, A. Kusoglu, K. G. Yager, and G. R. Stafford, *ACS Appl. Mater. Interfaces*, **7**, 17874–17883 (2015).

205. K. A. Page, A. Kusoglu, C. M. Stafford, S. Kim, R. J. Kline, and A. Z. Weber, *Nano Lett.*, **14**, 2299–2304 (2014).

206. S. A. Eastman, S. Kim, K. A. Page, B. W. Rowe, S. Kang, C. L. Soles, and K. G. Yager, *Macromolecules*, **45**, 7920–7930 (2012).

207. M. A. Modestino, A. Kusoglu, A. Hexemer, A. Z. Weber, and R. A. Segalman, *Macromolecules*, **45**, 4681–4688 (2012).

208. S. K. Dishari and M. A. Hickner, *ACS Macro Lett.*, **1**, 291–295 (2012).

209. A. Kusoglu, D. Kushner, D. K. Paul, K. Karan, M. A. Hickner, and A. Z. Weber,

Adv. Funct. Mater., **24**, 4763–4774 (2014).

210. A. Kusoglu, T. J. Dursch, and A. Z. Weber, *Adv. Funct. Mater.*, **26**, 4961–4975 (2016).

211. A. Siu, J. Schmeisser, and S. Holdcroft, *J. Phys. Chem. B*, **110**, 6072–6080 (2006).

212. C.-N. Sun, K. L. More, and T. A. Zawodzinski, *ECS Trans.*, **33**, 1207–1215 (2010).

213. T. A. Zawodzinski, T. E. Springer, F. Urlbe, and S. Gottesfeld, *Solid State Ionics*, **60**, 199–211 (1993).

214. Z. Luo, Z. Chang, Y. Zhang, Z. Liu, and J. Li, *Int. J. Hydrogen Energy*, **35**, 3120–3124 (2010).

215. M. Saito, K. Hayamizu, and T. Okada, *J. Phys. Chem. B*, **109**, 3112–3119 (2005).

216. K. Kidena, T. Ohkubo, N. Takimoto, and A. Ohira, *Eur. Polym. J.*, **46**, 450–455 (2009).

217. S. Ochi, O. Kamishima, J. Mizusaki, and J. Kawamura, *Solid State Ionics*, **180**, 580–584 (2009).

218. J. Peron, A. Mani, X. Zhao, D. Edwards, M. Adachi, T. Soboleva, Z. Shi, Z. Xie, T. Navessin, and S. Holdcroft, *J. Memb. Sci.*, **356**, 44–51 (2010).

219. E. H. Sanders, K. A. Mcgrady, G. E. Wnek, C. A. Edmondson, J. M. Mueller, J. J. Fontanella, S. Suarez, and S. G. Greenbaum, *J. Power Sources*, **129**, 55–61 (2004).
220. P. Choi, N. H. Jalani, and R. Datta, *J. Electrochem. Soc.*, **152**, E123–E130 (2005).
221. J. Li, K. G. Wilmsmeyer, and L. A. Madsen, *Macromolecules*, **42**, 255–262 (2009).
222. K. D. Kreuer, *Solid State Ionics*, **94**, 55–62 (1997).
223. Y. Sone, *J. Electrochem. Soc.*, **143**, 1254 (1996).
224. P. C. Rieke and N. E. Vanderborgh, *J. Memb. Sci.*, **32**, 313–328 (1987).
225. K. D. Kreuer, *J. Memb. Sci.*, **185**, 29–39 (2001).
226. K. D. Kreuer, *Solid State Ionics*, **97**, 1–15 (1997).
227. K. D. Kreuer, S. J. Paddison, E. Spohr, and M. Schuster, *Chem. Rev.*, **104**, 4637–4678 (2004).
228. H. K. Shim, D. K. Paul, and K. Karan, *Macromolecules*, **48**, 8394–8397 (2015).
229. M. A. Modestino, D. K. Paul, S. K. Dishari, S. A. Petrina, F. I. Allen, M. A. Hickner, K. Karan, R. A. Segalman, and A. Z. Weber, *Macromolecules*, **46**, 867–873 (2013).

230. L. Cindrella, A. M. Kannan, J. F. Lin, K. Saminathan, Y. Ho, C. W. Lin, and J. Wertz, *J. Power Sources*, **194**, 146–160 (2009).
231. M. Ikeda, N. Uematsu, H. Saitou, N. Hoshi, M. Hattori, and H. Iijima, *Polym. Prepr. Japan*, **54**, 4521–4522 (2005).
232. T. D. Gierke, G. E. Munn, and F. C. Wilson, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1687–1704 (1981).
233. W. Y. Hsu and T. D. Gierke, *J. Memb. Sci.*, **13**, 307–326 (1983).
234. W. Y. Hsu and T. D. Gierke, *Macromolecules*, **15**, 101–105 (1982).
235. E. J. Roche, M. Pineri, and R. Duplessix, *J. Polym. Sci.*, **20**, 107–116 (1982).
236. G. Gebel, *Polymer (Guildf.)*, **41**, 5829–5838 (2000).
237. B. Loppinet and G. Gebel, *Langmuir*, **14**, 1977–1983 (1998).
238. G. Gebel and B. Loppinet, *J. Mol. Struct.*, **383**, 43–49 (1996).
239. B. Loppinet, G. Gebel, and C. E. Williams, *J. Phys. Chem. B*, **101**, 1884–1892 (1997).
240. A. Z. Weber and A. Kusoglu, *J. Mater. Chem. A*, **2**, 17207–17211 (2014).
241. D. K. Paul and K. Karan, *J. Phys. Chem. C*, **118**, 1828–1835 (2014).
242. S. Kim, J. A. Dura, K. A. Page, B. W. Rowe, K. G. Yager, H. J. Lee, and C. L. Soles, *Macromolecules*, **46**, 5630–5637 (2013).

243. J. A. Dura, V. S. Murthi, M. Hartman, S. K. Satija, and C. F. Majkrzak, *Macromolecules*, **42**, 4769–4774 (2009).
244. H. G. Haubold, T. Vad, H. Jungbluth, and P. Hiller, *Electrochim. Acta*, **46**, 1559–1563 (2001).
245. S. M. Andersen, M. Borghei, R. Dhiman, V. Ruiz, E. Kauppinen, and E. Skou, *J. Phys. Chem. C*, **118**, 10814–10823 (2014).
246. X. Li, F. Feng, K. Zhang, S. Ye, D. Y. Kwok, and V. Birss, *Langmuir*, **28**, 6698–6705 (2012).
247. H. F. M. Mohamed, S. Kuroda, Y. Kobayashi, N. Oshima, R. Suzuki, and A. Ohira, *Phys. Chem. Chem. Phys.*, **15**, 1518–1525 (2013).
248. A. Ohira, S. Kuroda, H. F. M. Mohamedz, and B. Tavernier, *Phys. Chem. Chem. Phys.*, **15**, 11494–11500 (2013).
249. K. Kudo, R. Jinnouchi, and Y. Morimoto, *Electrochim. Acta*, **209**, 682–690 (2016).
250. K. Kudo and Y. Morimoto, *ECS Trans.*, **50**, 1487–1494 (2013).
251. H. Iden, A. Ohma, and K. Shinohara, *J. Electrochem. Soc.*, **156**, B1078 (2009).
252. B. T. Sneed, D. A. Cullen, K. S. Reeves, O. E. Dyck, D. A. Langlois, R. Mukundan, R. L. Borup, and K. L. More, *ACS Appl. Mater. Interfaces*, **9**, 29839–

29848 (2017).

253. M. Uchida, Y. Fukuoka, Y. Sugawara, N. Eda, and A. Ohta, *J. Electrochem. Soc.*, **143**, 2245 (1996).

254. M. Watanabe, M. Tomikawa, and S. Motoo, *J. Electroanal. Chem.*, **195**, 81–93 (1985).

255. S. M. Andersen, M. Borghei, R. Dhiman, H. Jiang, V. Ruiz, E. Kauppinen, and E. M. Skou, in *Carbon*, vol. 71, p. 218–228 (2014).

256. Q. Chen and K. Schmidt-Rohr, *Macromolecules*, **37**, 5995–6003 (2004).

257. C.-N. Sun, thesis, Case Western Reserve University (2011).

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