1. Introduction

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have received the most attention among the various types of fuel cells because of their ability to function at low temperatures and to generate high current densities. Furthermore, the compactness and light weight coupled with rapid start-up and commercialization potential have added to their appeal [1–5]. Fuel for these cells is generally gaseous H_2 or H_2 mixed with other gases (i.e., CO_2, H_2O and traces of CO) resulting from reforming of hydrocarbon fuels. Alcohols, such as ethanol and methanol, have also been used as fuels and such fuel cells are denoted as Direct Alcohol Fuel Cells (DAFC). Thus, PEMFCs have been widely studied and developed for powering various applications ranging from small electronic devices to electrical vehicles [6,7]. Consequently, interest continues in development of PEM fuel cell technology.

In PEM fuel cells, the most important part is the Membrane Electrode Assembly (MEA), where the electrochemical reactions occur at both anode and cathode. Electrocatalysts, typically Pt supported on conductive carbon, are coated onto the electrolyte membrane to catalyze the oxidation and reduction reactions at the anode and cathode, respectively. The two main methods for the fabrication of MEA are generally known as indirect and direct methods [1,2]. The indirect method is where the particulate Pt/C catalysts are applied to the Gas Diffusion Layer (GDL) prior to assembly with the electrolyte membrane. The direct method is when the particulate Pt/C catalysts are coated directly onto the electrolyte membrane. The direct method has also been called the thin film process or Catalyst Coated Membrane (CCM) process. Cheng et al. [8] has claimed that Pt utilization (where Pt utilization is defined as the concentration of surface Pt sites per gram Pt determined from cyclic voltammetry divided by the concentration of surface Pt sites per gram Pt determined by either selective chemisorption or transmission electron microscopy) was approximately 45% for the direct method, compared to 22% Pt utilization when the MEA was prepared by the indirect method. In agreement, Chun et al. [9] showed that for similar cell potentials, direct fabrication yielded current densities about twice those for an MEA fabricated by an

indirect method. Consequently, the direct method of MEA fabrication has become generally accepted and has steadily replaced different indirect methods [2,4,10,11].

Several techniques for direct MEA fabrication have been developed, including the methods of painting/spreading [12,13], decaling of catalysts [14], and spraying at high pressures [15,16]. With the painting/spreading and decaling methods it is difficult to control either Pt loadings or the uniformity of the coatings, and high pressure spraying also results in excessive production cost due to the loss of Pt/C particles during spraying. Consequently, electrodeposition [17,18] and a modified thin film method [19] have been proposed to control Pt loadings between 0.1 - 0.5 mg_{Pt}/cm^2 as well as uniformity of coating. However, with the modified, thin film method it is still difficult to control Pt particle sizes, and the Cl^- ions from the electrodeposition process ($PtCl_6^{2-}$ is the usual Pt source) can poison Pt surfaces and reduce catalytic activity [5]. Another emerging technique has been sputtering [20,21], which is able to lower Pt loadings between 0.01 and 0.04 mg/cm^2 and to control the uniformity of the Catalyst Layer (CL) with thicknesses between 5-10 nm. However, this technique gives relatively low Pt surface/volume ratios since the Pt exists as a continuous film and not discrete particles and has a poor adherence of Pt to the electrolyte membrane. Finally, sputtering requires vacuum conditions for deposition of the electrocatalyst (i.e., Pt, Ru or Co) onto the membrane; thus, cost and scalability become issues for commercial production.

More recently, high frequency spraying techniques have been developed for MEA fabrication, since they overcome many of the limitations of the previous methods. Millington [22] has reported the use of ultrasonic frequency (120 kHz) with a commercial spraying apparatus (Sono-Tek "Exacta-coat") to prepare coated assemblies using the indirect method, where GDLs were sprayed with electrocatalyst prior to hot pressing with the electrolyte membrane. For fuel cell performance with H_2 and O_2, the maximum power was about 11% higher than the value of 0.47 W/cm^2 for the hand painting technique; Pt loadings were 0.4 mg/cm^2 at the anode and 0.5 mg/cm^2 at the cathode. For direct MEA fabrication, the spraying technique was first reported by Huang [23], who also used a Sono-Tek "Exacta-coat" instrument

operating at a frequency of 48 kHz to coat a Pt/C electrocatalyst onto Nafion® 212 membrane. The Pt loading at the cathode was varied and compared to other direct fabrication methods. The minimum Pt loading at the cathode was lowered from 0.4 – 0.5 mg/cm^2 to 0.155 mg_{Pt}/cm^2 and was compared to 0.08 mg_{pt}/cm^2, obtained from the dual ion beam technique. Similarly, Zheng et al. [24] used an identical protocol to coat carbon-supported Ru catalysts onto Nafion® 212 membrane as the cathode. The maximum power of 127 mW/cm^2 for the H_2-Air system was obtained for a Ru loading of 0.14 mg_{Ru}/cm^2. While the work of Huang [23] and Zheng [24] focused mainly on the effect of lower Pt and Ru loadings for fuel cell performance, their efforts provided only limited fundamental information of MEA using both physical and chemical characterization methods.

The above summary suggests that in order to improve MEA fabrication, particularly using the ultrasonic spraying method, fundamental information is still required for optimal deposition of the active electrocatalyst onto the electrolyte membrane. In this communication, we report the results of MEA characterization fabricated by ultrasonic spraying using both electron microscopy and selective chemisorption methods. This marks the first time chemisorption has been conducted on actual Pt/C-coated membranes and provides the ability to compare with Pt site densities determined from electrochemical surface area (ESA) measurements. TEM was used primarily to investigate the physical bond between the conductive layer and electrolyte membrane prepared using this fabrication technique.

2. Experimental

2.1. MEA fabrication

An ultrasonic spraying apparatus operating at 20 kHz was used for the fabrication of all MEAs in this work. Figure 1 shows a diagram of the ultrasonic spraying apparatus. The spraying nozzle was perpendicularly positioned above the membrane at a fixed distance of approximately 2 centimeters. Commercially-obtained 20 wt% Pt/C catalysts from Johnson Matthey was used as the electrochemical catalyst for all MEAs. The catalyst inks were prepared in batch by using different Nafion contents, where

Nafion solutions of 5%wt (DuPont) of 300, 400, 500 and 600 μL were used, as shown in the first column of Table 1. The Pt loading of MEAs was maintained at 0.3 mg/cm^2 and the coated area on the electrolyte membrane was 23 cm^2 (4.8 cm x 4.8 cm). At this Pt loading, approximately 34.5 mg of the 20 wt% Pt/C catalyst was used for each MEA. From this, the weight percent of Nafion per Pt/C was calculated and is shown in the last column of Table 1, where the density of 5%wt Nafion solution is 0.85 g/cm^3. The catalyst inks for each percent weight of Nafion : Pt/C in Table 1 were made using 3 ml of tetrahydrofuran (THF) [AR grade, RCI Labscan Limited] and 1 ml of DI water as the solvent. The inks were dispersed in an ultrasonic bath for 25 minutes before coating. Nafion® XL from DuPont was used as the electrolyte membrane for all MEAs. The membranes were sprayed directly at 70°C to form the Catalyst Layer (CL). During spraying, the catalyst inks were fed into the ultrasonic nozzle at a rate of 0.3 ml/min using a motor-driven syringe pump (NE-300, New Era, Inc.). After spraying, the coated membrane was heated at 70°C at ambient pressure and air for 2 hours to evaporate the remaining solvent. The second side of the membrane was sprayed using the same ink composition and protocol. Thus, both sides of MEA should have similar compositions and properties.

2.2. Fuel cell performance

The non-hot-pressed MEA was placed into a single cell hardware using carbon cloth as the gas diffusion layer (GDL) having a one sided micro-porous layer (MPL) from CeTech (W1S1005). The single cell was assembled by tightening the bolts to 50 lb/in^2 and a fiberglass-silicone composite as the gasket. Cell temperature was maintained at 75°C and the relative humidity was about 95% at both anode and cathode. The back pressure of anode and cathode was ambient pressure (101.1 kPa absolute). The reactive gases were hydrogen and air for the anode and cathode, respectively. The stoichiometries of H_2 and Air were maintained at 1.2 and 3.0 times excess concentrations, which corresponding to the flow rate determined under current of 8.4 cm^3/min/amp and 50.0 cm^3/min/amp for H_2 and Air respectively. For open circuit voltage (OCV) measurements, the flow rate for H_2 was set at 50 cm^3/min, and that for air at 100 cm^3/min. An electronic load (890e, Scribner Associates, Inc.) was used to evaluate fuel cell

performance and to obtain the polarization curves. Before fuel cell tests, each MEA was conditioned by voltage oscillation from OCV to 0.6 V and then OCV to 0.45 V for two hours, retaining each potential for 30 seconds. Fuel cells were tested using the constant voltage mode; currents were measured at random, but constant, cell potentials. For each cell potential, the value was kept constant for 5 minutes before the current was recorded.

Cyclic voltammetry (CV) was applied to investigate the electrochemical reaction using the H_2 pump technique. The CV measurements were made while feeding humid N_2 to the cathode which functioned as the working electrode and humid H_2 to the anode that functioned as the counter/reference electrode. A Princeton Applied Research potentiostat/galvanostat model 263A was used to obtain CV measurements. The potential was examined from OCV to 1.14 V at a scan rate of 25 mV/sec and the current was recorded. The potential-current density profiles were recorded until reproducible profiles were obtained (typically after the second cycle).

2.3. Electron microscopy analysis

SEM images were taken using a model JEOL JSM-6335F operated at 15kV equipped with Energy Dispersive X-ray analysis (EDX). Cross-section images of the MEA were obtained and data for Pt, C, and F were recorded. The cross-sectioned samples were broken cleanly at liquid nitrogen conditions.

TEM images were taken using a JEOL JEM-2010 200 kV instrument equipped with Energy Dispersive X-ray analysis. An MEA was prepared using the Cryo-Microtome technique, where the temperature was reduced below the glass-transition temperature using liquid nitrogen. It was then cross-sectioned to give slices sufficiently thin to permit an electron beam to pass through the samples and gather images.

2.4. Chemisorption

Chemisorption of Nafion membranes coated on both sides with 20 wt% Pt/C was conducted by H_2 titration of O-precovered Pt using a Micromeritics AutoChem 2920 Automated Analyzer. The coated portion of the Nafion membrane was approximately 23 cm^2 (4.8 cm × 4.8 cm) on each side of the membrane for a total of 46 cm^2 surface. In order to fit into the 10 mm ID Pyrex chemisorption cell, the coated Nafion was cut (with 316 stainless steel scissors) into six strips that were approximately 8 mm in width × 5 cm in length and loaded into the tubular Pyrex chemisorption cell. Because the upper temperature limit for Nafion was ~130°C, the samples were pretreated at 75°C in flowing 10% H_2/balance Ar for 4 hrs before being cooled in flowing Ar to 40°C. The pretreatment temperature of 75°C in flowing 10% H_2 was sufficient to remove the passivation layer of O from the Pt surface for the samples that had been pre-reduced by Johnson-Matthey. Previous temperature programmed reduction studies of these samples showed facile reduction of the Pt-O surface passivation layer at 40°C. The sample was then exposed to flowing 10% O_2/balance He for 30 minutes before purging with flowing Ar for 30 minutes to remove residual gas phase O_2 from the chemisorption cell. The exposure to O_2 saturated the Pt surface sites to form Pt-O species. After the Ar purge, the sample was dosed with 0.518 cm^3 of 10% H_2/balance Argon until all Pt-O surface sites had been reacted to form H_2O and Pt-H species. Following three doses of no further H_2 uptake, the chemisorption was ceased. A second H_2 titration was then conducted by repeating the sequence of flowing 10% O_2/balance He for 30 minutes, flowing Ar for 30 additional minutes, and then H_2 titration of the Pt-O surface. Hydrogen consumption was quantitatively determined by means of a high sensitivity, thermal conductivity detector downstream from the sample cell. By conversion of H_2 uptake in (STP) ml to μmoles H_2 and the stoichiometry factor of 1.0 surface Pt/1.5 H_2 molecules (3/2 H_2 + Pt-O → H_2O + Pt-H), the concentration of surface Pt sites was readily achieved. Finally, a similar (blank) chemisorption sequence was conducted to ensure that no H_2 titration occurred on a Nafion-coated, Nafion membrane. To determine the concentration of Pt surface sites on the 20 wt%

Pt/C before coating on the Nafion membrane, 0.049 g of a powdered sample was subjected to the same pretreatment as the Nafion-coated sample and the concentration of active Pt surface sites was determined.

3. Results and discussions

3.1. Nafion loading

The Nafion : Pt/C percent weights were determined for optimal Nafion content in the catalyst ink for high-frequency spraying technique at constant platinum loadings of 0.3 mg_{Pt}/cm^2. The polarization curves in Figure 2 demonstrate four samples using Nafion : Pt/C of 37.0%wt, 49.3%wt, 61.6%wt, and 73.9%wt. This shows that the performance of MEAs with Nafion : Pt/C at 49.3%wt and 61.6%wt yielded almost similar profiles. The Nafion : Pt/C of 37.0%wt and 73.9%wt provide lower and the lowest performance, respectively.

From the above plots, constant cell voltages of 0.80, 0.65, and 0.50 Volt were selected for a plot of current density as a function of percent weight Nafion : Pt/C. The curves in Figure 3 indicate that the current density of all Nafion contents do not change significantly at a cell potential of 0.80 V, which represents the kinetic region. In the ohmic region (cell potential of 0.65 V), the current density of Nafion : Pt/C of 61.6%wt yields the highest current density of about 760 mA/cm^2. In the mass transport region (cell potential of 0.50 V), the maximum current density is about 1420 mA/cm^2 for a Nafion : Pt/C of 49.3%wt. These results indicate the overall best performance for Nafion : Pt/C between 49.3%wt and 61.6%wt. This result agrees with Millington et al. [22], who also used an ultrasonic spraying technique and found that a Nafion : Pt/C catalyst with weight ratio of 50% gave the highest current density. Compared to other methods of coating, Nafion : Pt/C ranging from 43 – 53 wt% for the painting [25,26] and high pressure spraying techniques [27] have been reported to give good performance.

The broad maxima in Figure 3 show that current density increases until the Nafion content reaches an optimal range of 50 – 62 %wt Nafion : Pt/C, indicating the importance of Nafion as an ion conductor to improve ion transportation in the CCL. At higher Nafion contents (i.e., 73.9%wt Nafion :

Pt/C), the current density decreases because the additional Nafion restricts access of Pt surface sites to reactant gases and hydrophilic Nafion likely entraps water in the CCL. Therefore, the Nafion content is one of the key factors that control fuel cell performance.

3.2. SEM and TEM images

An MEA with 49.3 wt% Nafion : Pt/C was analyzed by electron microscopy to examine the interface between the CCL and electrolyte membrane of the MEA. Figure 4(a) shows a cross section of MEA with a CCL thickness of approximately 15 μm on both sides of the electrolytic membrane. And the electrolytic membrane (i.e., Nafion XL from DuPont) has three layers, where the middle layer is the mechanical reinforcement with enhanced chemical stability, enabling improved membrane durability. The higher magnification shown in Figure 4(b) shows the CCL is highly porous because the Pt-supported carbon particles were highly and uniformly dispersed during high frequency spraying by the atomizer; this fabrication method built the CCL in a "layer by layer" methodology until the Pt loading reached 0.3 mg/cm^2. It is inferred that this fabrication technique enhances the diffusion of reactant gases (i.e. H_2 and O_2) to the Pt surface sites. Further, the pores should facilitate the transportation of the reaction product (water) out of the CCL to the GDL, which would alleviate electrode flooding at higher current densities.

Transmission electron microscopy was also used to analyze the interface between the CCL and electrolyte membrane in a more detailed manner, as shown in Figure 5. The images show the strong attachment between the electrolyte membrane and CCL as shown in Figures 5(a,b). These images also show that that the carbon-supported Pt particles (dark spots on the carbon support) are located in the CCL (upper portions of Figure 5(a,b)). At the higher magnification in Figure 5(b), the Ionomer Layer Film (ILF) is observed with a thickness of 100 - 200 nm. The ILF not only binds the CCL and electrolyte membrane, but also facilitates transfer of H^+ ions from the reaction zone to electrolyte membrane. Figure 5(b) also indicates that some of Pt/C catalyst particles are encapsulated in the ILF and are thus not able to

catalyze either the reduction or oxidation reaction. This blockage of Pt particles by the ionomer layer represents an activity loss mechanism of PEM fuel cells.

The high resolution TEM image in figure 5(c) shows the CCL of the membrane assembly. This image looks much like those of conventional Pt/C catalyst particles from previous work [28]. It is difficult to distinguish the ionomer in the CCL because of its transparent property to the electron beam of TEM. Thus, the EDX mode of analysis in Figure 6 was used during the SEM investigation to characterize the CCL images. Platinum, carbon, and fluorine (which represented the Nafion ionomer) were quantitatively analyzed and the results are shown in Table 2, where the first column is the observed element (i.e., carbon, fluorine, and platinum), the second column is the weight percentage of all observed elements, and the third column is the weight percentage of carbon and platinum only. The fluorine content was 26.6 wt% and was larger than that for platinum (12.5 wt%), which implies that the Nafion ionomer was spread throughout the CCL to assist transportation of H^+ ions at the Pt reaction sites to the electrolyte membrane. However, it also means that ionomers can cover and block platinum sites, preventing access to both H_2 and O_2 at the anode and cathode, respectively, to lower fuel cell performance. Therefore, the proper amounts of ionomers (Nafion) must be considered; in this work approximately 49 - 62 wt% Nafion : Pt/C gives the maximum power density. Finally, the EDX analysis in column 3 shows that the composition of carbon and platinum only are 83.0 wt% and 17.0 wt%, respectively, which agrees closely with the composition of the commercial 20 wt% Pt/C used in this work.

3.3. Chemisorption analysis

Pulse chemisorption spectra from H_2 uptake on a coated Nafion membrane, 20 wt% Pt/C powder, and an MEA (49.3 wt% Nafion: Pt/C), both before and after use, are shown in Figure 7. The spectrum for the Nafion membrane coated with 400 μL of 5% Nafion in Figure 7(a) shows no H_2 adsorption since even the first H_2 pulse exhibits the same height and peak area as all successive pulses. Conversely, the first seven H_2 pulses for the 20 wt% Pt/C (Figure 7(b)) were completely adsorbed before any H_2 was detected;

the first five H_2 pulses for the fresh MEA assembly (Figure 7(c) and used MEA assembly (Figure 7(d)) were completely adsorbed before H_2 was detected. The chemisorption of H_2 on Pt is considered complete when three consecutive H_2 pulses show no change in peak area. The cumulative volumes of H_2 uptake were quantified and converted to millimoles H_2 per gram of Pt as shown in third column of Table 3, where the standard deviation is calculated from 2 different analyses. For the 20 wt% Pt/C catalyst, the H_2 uptake is 1.98 millimole per gram of Pt from which a dispersion value (number of surface Pt atoms/total number of Pt atoms) was calculated to be 25.8%, corresponding to an average Pt particle diameter of 4.4 nm (assuming either hemispherical or spherical geometry).

Determination of the number of Pt surface sites per gram Pt is also shown in Table 3; these calculations require no assumption regarding Pt particle shapes or particle size distributions. The average concentration of Pt surface sites for catalyst particles is approximately 8.0×10^{20} sites per gram of Pt, while the concentration of accessible Pt sites for the fresh MEA is 3.8×10^{20} sites per gram of Pt, which means that 52% of potential Pt surface sites were lost when the Pt/C catalyst was fabricated onto the Nafion membrane. To the best of our knowledge, this marks the first time Pt surface sites in fabricated MEAs have been measured by chemisorption methods. The concentration of Pt surface sites after approximately 4 h of use is very similar to the concentration of Pt sites for the fresh sample, indicating that neither sintering of Pt particles nor poisoning by irreversible oxidation has occurred during this time period. Because of the inherent accuracy of chemisorption relative to other methods of measuring surface Pt site concentrations [28], the application of chemisorption for Pt-based fuel cells marks a significant improvement in helping to analyze the performance of such fuel cells. Intuitively, the loss of Pt surface sites is primarily due to the coverage of Pt by ionomer, which is consistent with the TEM micrographs in Figure 5. It is also obvious that further improvements and modifications are needed to minimize loss of Pt surface sites in the fabrication of MEAs. Minimization of the loss of Pt surface sites during MEA fabrication is just as important as ongoing studies to reduce Pt particle sizes in newer generation PEM fuel cells. The chemisorption process detailed in this study is an excellent analytical tool for these efforts.

Moreover, chemisorption analysis is advantageous for the measurement of active Pt sites for MEAs that are not fabricated from carbon-supported Pt catalysts, such as those resulting from ion beam, sputtering, or chemical vapor deposition methods.

3.4. Electrochemical surface area (ESA)

An MEA with 49.3 wt% Nafion : Pt/C catalyst was tested using cyclic voltammetry to measure the number of Pt surface sites from the electrochemical reaction. The cycling voltage ranged from open circuit voltage to 1.14 V (SHE), as shown in Figure 8. The adsorption and desorption of H^+ are calculated from potentials between 0.0 and 0.25 V for negative and positive current density, respectively [28,29]. The coulombic charges of H_2 adsorption (i.e. reduction reaction) increase as the upper potential increases [28]. Thus, desorption profiles (i.e. oxidation reaction) were used to evaluate Pt surface sites. Note that there are two partial peaks observed in the oxidation region at approximately 0.04 V and 0.12 V due to different Pt surface orientations as described in previous work [28].

The coulombic charge of positive current density was obtained by integrating current density with respect to cell potential from 0.0 V to 0.25 V. The double layer of positive current density (Figure 8) was also integrated with respect to the potential from 0.0 V to 0.25 V. The area under this profile is the coulombic change of the double layer. After subtraction of charge associated with the double layer, the charge of the desorption profile was approximately 0.183 coulomb, as indicated in Table 4. The mole ratio of H coulombic charge to H_2 was 2 : 1 for a two electron transfer ($2H^+ + 2e \rightarrow H_2$). The number of Pt surface sites from cyclic voltammetry was then calculated by assuming one H^+ per Pt surface site to give 1.6×10^{20} Pt surface sites per gram of Pt. The standard deviation values were calculated from 5 CV cycles of the MEA.

The Pt surface site concentration calculated from ESA is only 42% as large as the value of 3.8×10^{20} Pt sites g_{Pt}^{-1} determined from H_2 chemisorption. In fact, 80% of the potential Pt surface sites are lost when compared to the Pt surface site concentration for the 20 wt% Pt/C powder. However, H_2

chemisorption is a gas phase measurement done at dry conditions, where there are no complications from H_2O vapor. For the electrochemical reaction, the CV technique was conducted in a humid condition, likely resulting in condensation of vapor water in porous regions of the catalyst-coated layer (Kelvin condensation) which blocked access of H_2 to the Pt surface. In addition to potential water condensation, poor charge transfer in the CCL due to insufficient ionomer linkage between the Pt surface and the Nafion membrane can further limit the electrochemical reaction. Thus, the CV results are basically an implied measurement of Pt surface sites, depending on the extents of both charge transfer limitations and water condensation in the pores of the CCL. Therefore, Pt surface site concentrations of an MEA examined by CV are expected to be lower than those determined by H_2 chemisorption. In summary, electrochemical Pt catalysts lose active sites when they are fabricated as MEAs due to both coverage of the Pt surface by ionomer and the humid conditions and charge transfer limitations during operation of the MEA. In this study, 52% of the active Pt surface is lost by coverage with the ionomer and an additional 28% of the active Pt surface (80% - 52%) is lost due to conditions of fuel cell operation. Both of these Pt site loss mechanisms represent important areas of research for improvement of fuel cell operation. The combination of H_2 chemisorption and cyclic voltammetry have been identified and separated for these two mechanisms of activity loss. Future studies should address both issues, and H_2 chemisorption should be an integral component of these efforts.

4. Conclusions

Membrane electrode assemblies were fabricated directly onto an electrolyte membrane using a high frequency spraying technique developed in our laboratories. Fuel cell performance was dependent on Nafion content; maximum current densities at the ohmic and mass transport regions were found for compositions between 50 and 62 wt% of Nafion per Pt/C catalyst. Physical properties were also analyzed using electron microscopy to image cross sections of the MEA. From SEM analysis, the thickness of CCL was about 15 μm for both anode and cathode. The CCL was fabricated layer by layer, which generated pores for facilitating reactant gas (i.e. hydrogen and oxygen) diffusion. These pores also

improve water transport in the CCL and reduce cell flooding at higher current densities. From TEM analysis, the ionomer film layer between the CCL and electrolyte membrane was clearly observed. This supports the importance of Nafion content for H^+ transport in the reaction zone. However, higher Nafion loadings per Pt/C catalyst lowered fuel cell performance due to coverage of the Pt sites by Nafion. Platinum activities were quantified in term of site concentrations using H_2 chemisorption and cyclic voltammetry. At dry gas phase conditions, approximately 52% of the Pt surface sites in the MEA were lost due to coverage by the ionomer. For the electrochemical reaction (by cyclic voltammetry), an additional 28% loss of Pt surface sites occurred due to pore blockage by condensed water and the isolation of Pt to electronic and ionic conduction. Thus, in total 80% of the Pt sites present in the 20 wt% Pt/C electrocatalyst were lost during fabrication and operation of the membrane electrode assembly. Minimization of the loss of Pt surface sites by these two mechanisms is just as important as ongoing studies to reduce Pt particle sizes in newer generation PEM fuel cells. The chemisorption process detailed in this study is an excellent analytical tool for these efforts.

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