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Effect of the Cathode Catalyst Layer Thickness on the Performance in Direct Methanol Fuel Cells

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Abstract

Catalyst deposition control is one of the overlooked areas of fuel cell fabrication and research that can affect the overall performance and cost of the fuel cell to manufacture for mass production. The effect of the different individual catalyst layer thicknesses and loadings of the cathode compartment of a direct methanol fuel cell (DMFC) was investigated. The drawdown method was performed at thicknesses varying from 1 mil to 8 mils with platinum loadings ranging from 0.25 mg cm⁻² to 2.0 mg cm⁻². The membrane electrode assemblies (MEAs) with thicker individual layers (8 mil and 4 mil) performed better overall compared to the ones prepared with thinner individual layers (1 mil). The power density maxima for the different loading levels followed an exponential decrease of platinum utilization at the higher loading levels. The painted MEAs tended to display the similar performance characteristics as the drawdown MEA layers closest to the thickness at the respective loadings

Keywords: catalyst deposition, DMFC, layer thickness, platinum, spreading

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1. Introduction

As society's demand for energy is ever increasing with depleting fossil fuel reserves, alternative forms of energy need to be utilized more than ever. One way to help mitigate the demand is through the use of various types of fuel cells. Proton exchange membrane-based direct methanol fuel cells (DMFCs) are particularly attractive as they can be portable, run at low temperatures (<90 °C), and are energy dense due to methanol being a liquid unlike hydrogen, which is a gas [1–5]. Many practical applications have already been implemented with numerous patents worldwide, some based on our own work [6–11]. There are still some drawbacks that have hindered the fuel cell performance, particularly due to the relatively poor performance of platinum-based catalysts at the anode [12]. Pt/Ru-based catalysts can resist poisoning by the adsorbed carbon monoxide, enhancing the performance. However, ruthenium is also expensive and relatively unstable at oxidative potentials leading to ruthenium crossover through the membrane [13,14].

One of most widely studied electrochemical processes that often limits fuel cell performance is the oxygen reduction reaction (ORR) on the cathode. The energy required to break the molecular oxygen double bond is high [15], leading to a high activation overpotential and overall low performance of the fuel cell [16]. Another barrier involved with the cathode is the flooding of the electrode structure from water being produced from the ORR [17]. Much work has been done to mitigate these detriments [18–20]. Another factor that can contribute to this that is unique to the DMFC and other liquid-based PEMFCs is the electroosmotic drag of the water from the aqueous fuel solutions such as methanol or formic acid across the membrane from the anode-side to the cathode.

One of the most commonly overlooked aspects of the electrode structure is the intrinsic three-dimensional nature of the catalyst layer. Most of the catalytic screening involves half-cell electrochemical testing, which is in effect a pseudo two-dimensional study of the oxidation or reduction capabilities of the catalyst layer. The dynamics of the catalyst layer and membrane electrode assembly (MEA) of the fuel cell are considerably more complex than usually envisioned. In the fabrication of the MEA, variables

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pertaining to the catalyst layer such as the hot pressing temperature and pressure [21], the catalyst percentage and loading [22], catalyst ink pretreatment [23], ionomer content [24], pore size and structure [25], and multilayer design [26] can greatly affect the overall performance of the fuel cell. These factors are not accounted for in the half-cell electrochemical tests. In the past, the majority of the mathematical modeling of fuel cell MEAs has only accounted for various one- and two-dimensional aspects and processes such as porosity of the catalyst layer, effect of ionomer content, triple phase boundaries, and various reactant and product flow field designs [27–32]. There have, however, been a few three-dimensional modeling studies carried out pertaining to varied processes concerning DMFC performance including the cathode [33–35]. Such modeling has demonstrated that DMFC catalyst layer design is far more complex than previously thought. Each of the aforementioned aspects, and others that have yet to be studied, affect each other and ultimately the overall performance and lifetime of the MEA. Other factors that must be accounted for in liquid-based PEM fuel cells as mentioned is the electroosmotic drag of the water from the anode to cathode from aqueous reactant solution such as methanol in DMFCs. This can result in further flooding of the cathode and additional water transport and management issues involved in the oxygen reduction reaction (ORR). Further studies are required to decipher the role of the DMFC cathode layers and their thicknesses in the ORR.

Most often in catalyst design and MEA, the deposition of the catalyst onto the fuel cell electrode is overlooked and can greatly affect the overall performance. Various methods have been implemented including painting, sputtering [36,37], screen-printing [38,39], spraying [40,41], and spreading [42]. Our previous study involved the varying of individual catalyst layer thickness on the anode electrode of the DMFC. This showed a variation in performance in applying different individual layer thicknesses at a range of catalyst loadings on the anode electrode. Now, we have extended similar studies to the cathode electrode of PEM-based DMFCs and assessed the overall ORR performance in the fuel cell as it pertains to the individual layer thicknesses of the cathode catalyst layers.

2. Experimental

2.1. Preparation of Catalyst Slurry

A solution of 40% wt-Pt on carbon black (Alfa Aesar) was used as the catalyst for the cathode. A slurry was

created following a procedure by Park et. al [42] comprising of a 1:10:7:1:0.5 weight ratio of catalyst, Millipore water (Direct-Q UV, 18.2 MΩ), 5% Nafion® (Ion Power), DMSO (Macron), and isopropyl alcohol, respectively. The Nafion® ionomer ratio was set to 26% based on the equation:

$$W_{\text{Naf}} / (W_{\text{Naf}} + W_{\text{Cat}}) \times 100 \quad (1)$$

where W_{Naf} is the weight of the Nafion® and W_{Cat} is the weight of the catalyst including the carbon support [43,44]. The slurry was sonicated and stirred until a homogenous solution was formed.

A slurry of 20% wt-Pt and 10% wt-Ru on Carbon Black (Alfa Aesar) with Nafion®, was used as the catalyst for the anode with the same chemical components and ratios for the slurry as the cathode. The slurry was sonicated and painted on the anode with a Pt/Ru loading of 1.9 mg cm⁻².

2.2. Deposition of the Catalyst

The drawdowns were performed via a square drawdown bar (BYK) with 8 different thicknesses ranging from 1 mil to 8 mils (1 mil = 25.4 μm) as described in our previous study [45]. Drawdowns were performed at layer thicknesses of 1, 4, and 8 mils at Pt loadings of 0.25, 0.50, 1.0, and 2.0 mg cm⁻², respectively, on a Toray carbon paper (E-Tek, TGH-060, 6% wet-proofing) with an active surface area of 5 cm². The catalyst was dried in the oven at 110 °C after each coat and the process repeated until the desired platinum loading for the sample was achieved. The catalyst slurry was also painted on the cathode with a paint brush and dried in the oven in the same manner in between each coat with the same platinum loadings as previously mentioned.

2.3. Fuel Cell Fabrication

The protonated form of Nafion-117® was cut into 10.16 cm x 10.16 cm pieces, sandwiched between the anode and cathode, and hot pressed at 140 °C for 5 minutes at 250 kilograms of force. The resulting MEA was then fitted inside the fuel cell assembly and hydrated overnight with Millipore water at 60 °C.

2.4. Scanning Electron Microscope (SEM) Measurements

SEM measurements were carried out with a JEOL JSM-7001F electron microscope with an acceleration voltage of 10.0 kV. SEMs of the cross sections were taken from the middle of the electrode aligned vertically on the plate to measure the thickness as well

as to examine the cross-section of the catalyst layer on the carbon paper.

2.5. Electrochemical Measurements

Polarization measurements were performed using a Fuel Test System 890B (Schriber Associates Inc.). The fuel cells were tested with 0.5 M methanol (Macron) solution flowing at 90 mL min⁻¹ at 60 °C in the anode compartment and ultrapure O₂ (99.994%) or air flowing at 100 mL min⁻¹ in the cathode compartment. The fuel cell measurements were carried out at 50 °C. The discharge current was scanned from the open circuit voltage (OCV) to zero volts.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed with a Solartron SI 1287 and SI 1260 Impedance-Phase Analyzer. EIS measurements were performed under the same conditions as the polarization measurements. Impedance measurements were taken at 0.3 V versus OCV with an AC amplitude of 100 mV with frequencies ranging from 100 kHz to 10 mHz. The resulting impedances were analyzed and fitted from the Z-Plot software (Schriber Associates Inc.).

Electrochemically active surface areas (ECSAs) of the cathode layer catalysts were measured by the CV method prescribed by Huang et al [46]. Millipore water was pumped through the cathode compartment at 100 mL min⁻¹, while ultrapure H₂ gas (99.999%) was flowed through the anode compartment at 100 mL min⁻¹ that was used as the reference hydrogen electrode (RHE). The cell temperature was kept at 60 °C for testing. The cell was cycled at a potential of 0.0 V to 1.0 V versus RHE at a rate of 50 mV s⁻¹ using a Solartron SI 1287.

3. Results and Discussion

3.1. Catalyst Layer Deposition

The catalyst layers consisted of 8 mil, 4 mil, and 1 mil drawdown layer thicknesses as well as painted layers. Each different drawdown was performed with platinum loading targets of 0.25, 0.50, 1.0, and 2.0 mg cm⁻². Table 1 shows the number of layers deposited for each sample. The platinum loadings for each of the

MEAs were close to the target loadings and the difference was taken into account by the normalization of the fuel cell performances.

Table 1. Number of layers deposited for each of the drawdown thicknesses at each of the Pt loading levels.

3.2. SEM Measurements

Figures 1a-d show the cross sections of the electrodes for the different drawdown thicknesses. Each electrode was coated with two layers of the respective drawdown thickness. The first layer acted to penetrate the porous carbon electrode while the second layer built upon the top of the electrode. The different thicknesses of the subsequent layers can be seen protruding from the carbon paper. The thicknesses for the 8 mil, 4 mil, 1 mil, and painted layers were measured to be about 25 μm, 15 μm, 5 μm, and 15 μm, respectively. Figures 2a-d show the SEMs of the various layer thicknesses from the 4 mil drawdowns reproduced from the targeted loadings described in Table 1. As the number of layers increases, the thickness of the solid blocks of catalyst protruding from the electrode increases. The measured thickness of the layers protruding from the porous carbon electrode in these samples was measured to be about 15 μm, 25 μm, 40 μm, and 60 μm for the 2, 3, 4, and 8 layers, respectively.

3.3. Polarization Measurements

Figures 3a-d show the polarization curves for the MEAs with O₂ flowing through the cathode. The 4 mil MEA shows superior performance with all catalyst loadings except for 2.0 mg cm⁻². In Figure 3c, the polarization curve of the painted layers overlaps with the 8 mil polarization curve. The maximum power densities for the MEAs with both O₂ and air flowing in the cathode are shown in Figure 4a. At each drawdown layer thickness, the data follows a logarithmic trend for both the O₂ and air with a relatively large increase in maximum power density between the 0.25 mg cm⁻² and

Thickness	0.25 mg cm ⁻²	0.5 mg cm ⁻²	1.0 mg cm ⁻²	2.0 mg cm ⁻²
8 mil	1	2	3	6
4 mil	2	3	4	8
1 mil	3	4	9	15
Painted	2	3	7	16

Fig. 1. SEM images of the cross sections of 2 layers deposited with drawdown thicknesses of a) 8 mil, b) 4 mil, c) 1 mil, and d) painted.

Fig. 2. SEM images of the cross sections of 4mil drawdowns with a) 2 layers, b) 3 layers, c) 4 layers, and d) 8 layers.

0.50 mg cm⁻² loadings and a slight increase in maximum power density from the 0.50 mg cm⁻² up to the 2.0 mg cm⁻² loadings. This concurs with the results from our previous work in which the drawdowns were performed on the anode [45].

The difference in power densities between the individual layers for each respective loading varies. For example, the 4 mil layers display a 95% increase in power density over the 1 mil layers at a loading of 0.25 mg cm⁻². This decreases to around 5% at the 2.0 mg cm⁻² catalyst loading.

Due to the minute differences in catalyst loadings between the respective layer thicknesses, the normalized power densities (in mW mg⁻¹) were calculated and plotted in Figure 4b. An exponential decay trend is observed as the Pt loadings were increased, indicating a loss in catalyst utilization as reported in earlier research [45,47]. This trend can be due to the penetration depth of the gases flowing in the cathode side of the MEA. At higher loadings, only a fraction of the catalyst layer is electrochemically active leading to lower catalyst utilization and only minor increases in cell performance [48]. The 4 mil drawdown MEAs exhibit the highest normalized maximum power density overall whereas the 1 mil

drawdown MEAs exhibit the lowest normalized maximum power density. Interestingly, the performance of the painted MEAs, mimics the performance of the MEAs of the drawdowns that have the closest number of layers for a given catalyst loading. For example, the performance of the painted MEAs at the lower loadings is most similar to that of the 4 mil drawdown MEAs. Both MEAs have the same number of layers at the lower loadings. The difference in the normalized power densities between the various layer thicknesses also varies through the respective loadings. For example,

Fig. 3. Polarization curves of the fuel cells at Pt loadings of a) 0.25 mg cm⁻²; b) 0.50 mg cm⁻²; c) 1.0 mg cm⁻²; and d) 2.0 mg cm⁻².

the 4 mil layers display a 70% increase in normalized power density at the 0.25 mg cm⁻² loading compared with the 1 mil layers, which decreases to 10% at the 2.0 mg cm⁻² loading.

Another factor worth noting is the comparison of

the performance of the MEAs between the O₂ and air

flowing through the cathode. Figure 4a shows the

Fig. 4. Summary of the a) Maximum Power Densities (in mW cm⁻²); and b) Maximum Normalized Power Densities (in mW mg⁻¹ Pt) of the MEAs. The solid markers represent O₂; the hollow markers represent air flowing in the cathode.

difference in the maximum power densities between the O₂ and air for each of the MEAs to be around 8-9 mW cm⁻² at each of the respective loadings regardless of the individual layer thicknesses. In Figure 4b, the difference in the normalized maximum power densities decreases as the catalyst loading increases. This shows a better utilization of the oxygen in the air in the catalyst layers at higher loadings. For instance, the 4 mil layers run with O₂ displayed a 103% increase in normalized power density, when compared to running with the air at the 0.25 mg cm⁻² loading. At the 2.0 mg cm⁻² loading, this factor decreases to 23%.

3.4. EIS Measurements

Figures 5a-d show the Nyquist plots for the impedance of the MEAs. The graphs were analyzed with an equivalent circuit model shown in Figure 6c. In this model, R_{ele} , R_{kin} , and R_{mas} represent the membrane, charge transfer, and mass transfer resistances, respectively. Since the semicircles for the impedances have a depressed shape, the capacitor elements have been replaced with the constant phase elements CPE₁ and CPE₂ showing the pseudo-distributive nature of the catalyst layers. L_1 and L_2 represent the inductances caused from the connecting wires and equipment. W_s

Fig. 5. EIS measurements of the fuel cells at Pt loadings of: a) 0.25 mg cm^{-2} ; b) 0.50 mg cm^{-2} ; c) 1.0 mg cm^{-2} ; and d) 2.0 mg cm^{-2} . The solid and hollow marks represent the O_2 and air experimental results respectively; the lines representing the fitted circuit.

represents the Warburg element for the finite diffusion of the materials through the catalyst layers. At the lower loadings, the MEAs for both the O_2 and air exhibit a

pronounced double semi-circle. As the loadings increase, the double semi-circles become less pronounced and finally resembles one depressed semi-circle. A possible explanation for this could be due to

the porosity of the cathode catalyst layers. At higher loadings, the impedance spectra resemble those of a thick porous electrode [49] while at lower loadings, the layers are thinner leading to less impedance to the mass transport of the gases and the resulting products.

Figures 6a&b, give a summary of the charge and mass transfer resistances of the fuel cells calculated from the equivalent circuit model. The overall trend for both the charge and mass transfer resistances is a steady decrease with increased catalyst loadings. This can be due to the penetration depth of the reactants in the cathode. At the higher loadings, there is less active catalyst exposed to the reactant leading to less overall diffusion through the catalyst layers. This decrease in diffusion leads to both a decrease in charge and mass transfer as the catalyst loadings increase. There is also a difference in the charge and mass transfer resistance between the layer thicknesses at various loadings. For example, at 0.25 mg cm^{-2} , the 4 mil layers exhibit a 23% decrease in

Fig. 6. Summary of the a) charge transfer resistances; b) mass transfer resistances of the fuel cells at the different Pt loading levels from the circuit fit; and c) the equivalent circuit. The solid and hollow marks represent the O_2 and air experimental results, respectively.

charge transfer resistance and a 32% decrease in mass transfer resistance compared to the 8 mil layers. At 2.0 mg cm^{-2} , the charge transfer resistance increased by 7% and the mass transfer resistance decreased by 22%. This stems from the structure of the triple phase boundary in the catalyst layers, where the catalyst, ionomer, and electrolyte come into contact. As the loadings increase, the relative area of the triple phase boundary reaches a maximum where no other charge and mass transfer can occur. Another aspect worth noting is the cathodes with air flowing through have higher charge and mass transfer resistances than do those with the O_2 . This is due to the increased diffusion necessary for the oxygen through both the nitrogen present in the air and the water in the cathode to reach the active catalytic sites [50,51].

Interestingly, the impedances of the painted MEAs seem to mimic the impedances of the drawdown MEAs that have the most similar number of layers at a certain catalyst loading. For example, at the 1.0 and 2.0 mg cm^{-2} loadings, the 1 mil MEAs have the same number of layers as the painted MEAs. In Figures 5c&d, the impedance spectra for the 1 mil and painted MEAs are the most similar. This supports the idea that individual layer thicknesses have an effect on the performance and chemical processes of the DMFCs.

One reason for the differences in charge and mass transfer differences as was explained in our previous work is the tortuosity of the catalyst layers in the MEAs [45]. Thinner individual layers can lead to higher tortuosity and higher mass transfer resistance of

the O₂ (and air) in the cathode catalyst layers [52,53]. Another possible detrimental aspect linked with the higher tortuosity is the flooding caused from both the electroosmotic drag across the membrane from the water in the aqueous methanol solution from the anode as well as from the oxygen reduction reaction. The higher tortuosity in the catalyst layers leads to longer more winding pathways for the water to travel leading to an increase of flooding in the cathode compartment. This can possibly be a significant detriment to the overall fuel cell performance.

3.5. CV Measurements

Figures 7a-d show the CVs of the different fuel cells normalized with respect to the Pt loadings of the cathode. The electrochemically active surface areas (ECSAs) were calculated from the hydrogen adsorption region located roughly between 0.0 V and 0.3 V vs. RHE. The region at 0.3 V corresponds to the double layer capacitance region and is subtracted from the area above the curve in the hydrogen adsorption region [54]. Figure 8 shows the summary of the normalized ECSAs. The general trend seen here is a decrease in ECSA with the increase of catalyst loading. One way to explain this

Fig. 7. CV scans of the fuel cell cathode with catalyst loadings of a) 0.25 mg cm⁻²; b) 0.50 mg cm⁻²; c) 1.0 mg cm⁻²; and d) 2.0 mg cm⁻².

is from the triple phase boundary, which is the section of the catalyst layer, wherein the catalyst, ionomer, and electrolyte are in contact [55]. As the overall catalyst loadings increase in the MEAs, more of the catalyst

Fig. 8. Summary of the normalized ECSAs of the fuel cells at the different loadings.

becomes inactive, leading to lower ECSA values for the catalyst. Another trend observed from this is the difference in the ECSA values between the individual layer thicknesses at the various loadings. There is a considerable difference in the lower loadings, whereas this difference becomes negligible at higher loadings. For example, the painted layers show a 19% increase in ECSA from the 1 mil layers at the 0.25 mg cm⁻² loading. This figure decreases to 8% at 1.0 mg cm⁻² and down to 5% at 2.0 mg cm⁻². This again stems from the triple phase boundary, where at the higher loadings (above 0.50 mg cm⁻²), the catalyst is saturated beyond the penetration boundary where no reactants will reach the catalyst.

4. Conclusions

One of the most widely studied reactions in electrochemistry is the ORR. However, most of the studies focus of the half-cell electrochemical measurements with the catalysts being studied on a two-dimensional scale. Numerous variables regarding the overall complexity of the fuel cell layers and electrochemical processes still need to be taken into account to assess the actual viability of the catalyst in the MEA of the fuel cell. Some of these include the overall thickness of the catalyst layer, porosity of the catalyst and ionomer, effect of temperature and pressure with the hot pressing of the MEA, effect of the ionomer and content on catalytic activity, and numerous others. There are variables that are still unknown in this complex three-dimensional system

that cannot be accurately ascertained with either testing or modeling in two-dimensional simulations or electrochemical cells. The overall performance of a direct methanol fuel cell is highly complex, involving numerous variables that are only now starting to be discovered and understood. Our previous study showed the variation in individual anode catalyst layers that can affect the performance and other aspects such as charge transfer at various catalyst loadings. This same concept has now been extended to the cathode catalyst layer of the DMFC as was demonstrated in this study. For instance, the 4 mil layer thickness displayed a 95% increase in power density over the 1 mil layers at a loading of 0.25 mg cm⁻². This increase in performance decreases to around 5% at the 2.0 mg cm⁻² loading. Further research and MEA testing is still needed to uncover and optimize these novel parameters and conditions in order to achieve DMFCs with superior performance.

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