

**MODIFIED CATALYST LAYER INTERFACES FOR HIGHER UTILIZATION AND  
IMPROVED OPERATIONAL FLEXIBILITY OF LOW LOADING POLYMER  
ELECTROLYTE FUEL CELL CATALYST LAYERS**

by

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## Abstract

Featuring low operational temperature and high-power density, polymer electrolyte membrane fuel cells (PEMFCs) have become the most researched and used fuel cell for the emerging automotive applications. To further promote the competitiveness of the fuel cell, improvement in operational flexibility to enable fuel cell to maintain its performance under various conditions is critical. The approach taken here was to modify the membrane electrode assembly (MEA) structure, particularly the interfaces of the cathode catalyst layer. Two interfaces were studied and modified, namely the membrane | cathode catalyst layer (CCL) and the CCL | microporous layer (MPL) interfaces.

Firstly, the interface of the membrane and CCL was modified by addition of a thin, dense Pt layer in the membrane subsurface ( $<250$  nm). This Pt layer was physically and electrochemically characterized. The application of this platinized membrane with a loading  $<20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  demonstrates a comparable performance to the baseline but improves the performance at low humidity conditions due to a better humidification of the membrane and catalyst layer. The performance benefits are also maintained during a longer humidity cycling test. This new platinized membrane structure also shows reduction in hydrogen crossover (up to 65%) with the loading studied ( $<80 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ).

Secondly, the interface of the CCL and MPL was modified by applying a modified MPL directly on the CCL. A new MEA architecture with a modified MPL consisting of  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  reduces gaps at this interface, and hence reduces cell contact resistance by 31% and increases the limiting

current density by about 10%. The modified MPL with  $0.8 \text{ mg cm}^{-2}$  Acetylene Black shows the highest performing MEA with  $\sim 37\%$  maximum power density gain, while the optimum loading for VC-based MPL is  $\sim 0.4 - 0.8 \text{ mg cm}^{-2}$  yielding  $\sim 27\%$  maximum power density gain at 100% RH. The loading of  $0.8 \text{ mg cm}^{-2}$  appears to be the threshold to enable the modified MPL to have performance benefits under low humidity. The long-term performance under low and high humidity showed that MEAs with additional modified MPL have a more stable and lower performance drop than for MEAs with a conventional MPL only.



## **Lay Summary**

Hydrogen fuel cells have gained significant interest as a more sustainable device for automotive and other applications due to their higher efficiency. To further improve the performance of the hydrogen fuel cell, a new membrane electrode assembly (MEA) structure is developed in this research. The MEA is the critical unit of the fuel cell and consists of multi-layer materials that do the conversion of hydrogen with oxygen or air to produce water and electricity. Due to its multilayer structure, the interfaces between the layers are critical and often cause deterioration of the performance, particularly at the more extreme conditions (too wet or too dry). The application of a low loading electroless Pt layer at the membrane and catalyst layer interface and a hydrophobic modified microporous layer to the catalyst layer and gas diffusion medium interface have demonstrated performance improvement under various conditions, and hence improve fuel cell operational flexibility.

## Preface

The work presented in this thesis, including literature review, experimental design and execution, data analysis and interpretation, and thesis writing, was completed by Lius Daniel under direct supervision of Professor David Wilkinson at the Department of Chemical & Biological Engineering, the University of British Columbia. This research is also part of collaboration with Johnson Matthey Fuel Cell in the UK. The half-cell and floating cell used in this research were designed and initially developed by Dr. Blaise Pinaud and Greg Afonso. Dr. Blaise Pinaud also contributed to the early phase of the experimental design of the work written in Chapter 3 and Chapter 4. Three UBC Chemical Engineering undergraduate students, Melissa Beaulac, Harneet Kaur, and Tracy Nguyen, assisted characterizations used in this thesis. Melissa contributed to the XRF and ICP characterization in Chapter 3, while Harneet and Tracy performed electrochemical and physical characterizations in Chapters 3 and 4.

Chapter 3 of this thesis has been published as:

- Daniel, L.; Bonakdarpour, A.; Wilkinson, D. P. Low-Loading Electrolessly-Deposited Pt Nafion Membranes for PEMFC Applications: Enhancing the Operational Flexibility.” *Journal of Power Sources*. **2020**, 471, 228418. I conducted all design, testing, collected the data and analysis of the results, and wrote the manuscript under the guidance of D.P. Wilkinson. A. Bonakdarpour assisted with manuscript writing, data analysis and experimental design.
- Daniel, L.; Bonakdarpour, A.; Sharman, J.; Wilkinson, D. P. “New CCL|MPL Architecture Reducing Interfacial Gaps and Enhancing PEM Fuel Cell Performance.” *Fuel Cells*. **2020**, 2, 224-228. I conducted all design, testing and analysis of the results and wrote the manuscript under the guidance of D.P. Wilkinson. J Sharman provided useful discussion and suggestions with regard to the experimental design. A. Bonakdarpour assisted with manuscript writing and experimental design.

Part of Chapter 4 has been published as:

- Daniel, L.; Bonakdarpour, A.; Wilkinson, D. P. “Relationship between Electroless Pt Nanoparticle Growth and Interconnectivity at the Membrane Interface: Implications for Fuel Cell Applications.” *ACS Appl. Nano Mater.* **2019**, 2, 3127–3137. I conducted all design, testing and analysis of the results, and wrote the manuscript under the guidance of D.P. Wilkinson. A. Bonakdarpour assisted with manuscript writing, data analysis and experimental design.

Part of Chapter 4 is currently in preparation for submission as:

- Daniel, L.; Bonakdarpour, A.; Govindarajan, R.; Wilkinson, D.P. “Modified CCL|MPL Interfacial Structure for Improved Low Pt Loading PEM Fuel Cell Performances” (in preparation).

The author was also contributed to a publication on half-cell development, which is also used in this research:

- Pinaud, B.A., Bonakdarpour, A., Daniel, L., Sharman, J., and Wilkinson, D.P. “ Key Considerations for High Current Fuel Cell Catalyst Testing in an Electrochemical Half-Cell.” *J. Electrochem. Soc.* 2017, 164, 4, F321–F327. I assisted B.A. Pinaud with the half-cell testing and MEA testing in a fuel cell hardware and data analysis comparing the performance from half-cell and fuel cell. I later modified the half-cell design and used it for CCM electrochemical characterization.

The work has also been presented at the following conferences by the author:

- Daniel, L., Bonakdarpour A., Wilkinson D.P., “The Impact of Electroless Thin Pt Layer Deposition in Nafion Membranes on H<sub>2</sub>/O<sub>2</sub> PEM Fuel Cell Performance”, The Electrochemical Society Conference 233<sup>rd</sup> Seattle, 2018.
- Daniel, L., Pinaud, B.A., Sharman, J., Wilkinson D.P., “Application of Electroless Deposition to Build Integrated Catalyst Architectures for PEM Fuel Cells”, Johnson Matthey Academic Conference, 2016.

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## List of Symbols

|                          |                                                                  |
|--------------------------|------------------------------------------------------------------|
| $A$                      | Active area ( $\text{m}^2$ )                                     |
| $a$                      | Cross-sectional area ( $\text{m}^2$ )                            |
| $a$                      | Chemical activity                                                |
| $b$                      | Tafel slope ( $\text{mV dec}^{-1}$ )                             |
| $C_{r,s}$                | Concentration of reactant at the surface (M)                     |
| $C_{r,b}$                | Concentration of reactant in the bulk region (M)                 |
| $D$                      | Crystal size in Scherrer equation (nm)                           |
| $E$                      | Potential or voltage (V)                                         |
| $E^0$                    | Potential at standard condition (V)                              |
| $E^0_{\text{cell}}$      | Cell potential at standard condition (V)                         |
| $F$                      | Faraday constant ( $\text{C mol}^{-1}$ )                         |
| $G$                      | Gibbs free energy (J)                                            |
| $\hat{g}$                | Gibbs free energy per mol ( $\text{J mol}^{-1}$ )                |
| $\hat{g}^0$              | Standard state Gibbs free energy per mol ( $\text{J mol}^{-1}$ ) |
| $H$                      | Enthalpy ( $\text{J mol}^{-1}$ )                                 |
| $H_{\text{combustion}}$  | Enthalpy of Combustion ( $\text{J mol}^{-1}$ )                   |
| $[\text{H}^+]$           | Concentration of proton (M)                                      |
| $i_0$                    | Exchange current density ( $\text{mA cm}^{-2}$ )                 |
| $i_{\text{crossover}}$   | Crossover current density ( $\text{mA cm}^{-2}$ )                |
| $i_L$                    | Limiting current density ( $\text{mA cm}^{-2}$ )                 |
| $I$                      | Current (A)                                                      |
| $j$                      | Crossover molar rate ( $\text{mol cm}^{-2} \text{s}^{-1}$ )      |
| $k$                      | Reaction constant                                                |
| $m$                      | Loading ( $\mu\text{g cm}^{-2}$ )                                |
| $M_{\text{Pt-grain}}$    | Pt loading mass density ( $\mu\text{g cm}^{-2}$ )                |
| $N_{\text{Pt-grain}}$    | Number of Pt grains                                              |
| $P$                      | Pressure (Pa)                                                    |
| $P_{\text{utilization}}$ | Utilization of Pt particles (%)                                  |

|                               |                                                                       |
|-------------------------------|-----------------------------------------------------------------------|
| $r_{\text{Pt-grain}}$         | Pt crystallite size (nm)                                              |
| $R_{\text{ohmic}}$            | Ohmic resistance ( $\Omega \text{ cm}^2$ )                            |
| $S$                           | Entropy ( $\text{J K}^{-1}$ )                                         |
| $\hat{S}$                     | Entropy per mol ( $\text{J K}^{-1} \text{ mol}^{-1}$ )                |
| $\hat{S}^o$                   | Standard state entropy per mol ( $\text{J K}^{-1} \text{ mol}^{-1}$ ) |
| $S_{\text{BET}}$              | Surface area determined by BET ( $\text{m}^2 \text{ g}^{-1}$ )        |
| $T$                           | Temperature (K)                                                       |
| $V_c^{\text{OCV},t}$          | Thermodynamics or Nernstian OCV (V)                                   |
| $V_c^{\text{OCV},m}$          | Measured OCV (V)                                                      |
| $\Delta V_{\text{Pt/PtO}}$    | OCV change contributed by Pt/PtO mixed potential (V)                  |
| $\Delta V_{\text{crossover}}$ | OCV change contributed by hydrogen crossover (V)                      |
| $V_{\text{Pt-grain}}$         | Volume of Pt grain ( $\text{nm}^3$ )                                  |
| $V_{\text{micro}}$            | Micropores volume ( $\text{cm}^3 \text{ g}^{-1}$ )                    |
| $V_{\text{total}}$            | Total volume ( $\text{cm}^3 \text{ g}^{-1}$ )                         |
| $W_{\text{Pt-grain}}$         | Total weight of deposited Pt ( $\text{g}_{\text{Pt}}$ )               |

## Greek

|           |                                                               |
|-----------|---------------------------------------------------------------|
| $\mu$     | Chemical potential                                            |
| $\mu^o$   | Chemical potential at standard state conditions               |
| $\lambda$ | $K\alpha$ radiation wavelength of copper                      |
| $\theta$  | Radian                                                        |
| $\sigma$  | Conductivity                                                  |
| $\pi$     | Phi                                                           |
| $\Gamma$  | Charge required to reduce a monolayer of hydrogen on platinum |
| $\alpha$  | Transfer coefficient                                          |
| $\Omega$  | Resistance                                                    |
| $\lambda$ | Stoichiometry                                                 |
| $\eta$    | Overpotential                                                 |
| $\eta$    | Theoretical efficiency                                        |

## List of Abbreviations

|                |                                                          |
|----------------|----------------------------------------------------------|
| <b>AB</b>      | Acetylene Black                                          |
| <b>ACL</b>     | Anode Catalyst Layer                                     |
| <b>BEV</b>     | Battery Electric Vehicle                                 |
| <b>BP</b>      | Black Pearl 2000                                         |
| <b>CCL</b>     | Cathode Catalyst Layer                                   |
| <b>CCM</b>     | Catalyst Coated Membrane                                 |
| <b>CCS</b>     | Carbon Capture and Storage                               |
| <b>CL</b>      | Catalyst Layer                                           |
| <b>CV</b>      | Cyclic Voltammetry                                       |
| <b>ECSA</b>    | Electrochemically Active Surface Area                    |
| <b>EIA</b>     | Energy Information Administration                        |
| <b>EV</b>      | Electric Vehicle                                         |
| <b>FCC</b>     | Face-centered Cubic                                      |
| <b>FCEV</b>    | Fuel Cell Electric Vehicle                               |
| <b>GDE</b>     | Gas Diffusion Electrode                                  |
| <b>GDL</b>     | Gas Diffusion Layer                                      |
| <b>HFR</b>     | High Frequency Resistance                                |
| <b>HHV</b>     | High Heating Value                                       |
| <b>HOR</b>     | Hydrogen Oxidation Reduction                             |
| <b>ICEV</b>    | Internal Combustion Electric Vehicle                     |
| <b>ICP-OES</b> | Inductively Coupled Plasma Optical Emission Spectrometry |
| <b>I-R</b>     | Impregnation-reduction                                   |
| <b>LHV</b>     | Low Heating Value                                        |
| <b>LSV</b>     | Linear Sweep Voltammetry                                 |
| <b>MEA</b>     | Membrane Electrode Assembly                              |
| <b>MPL</b>     | Microporous Layer                                        |
| <b>MT</b>      | Mass Transport                                           |
| <b>OCV</b>     | Open Circuit Voltage                                     |

|              |                                                       |
|--------------|-------------------------------------------------------|
| <b>OER</b>   | Oxygen Evolution Reaction                             |
| <b>ORR</b>   | Oxygen Reduction Reaction                             |
| <b>PEIS</b>  | Potentiostatic Electrochemical Impedance Spectroscopy |
| <b>PEM</b>   | Proton Exchange Membrane                              |
| <b>PEMFC</b> | Proton Exchange Membrane Fuel Cell                    |
| <b>PFSA</b>  | Perfluorosulfonic Acid                                |
| <b>PGM</b>   | Platinum Group Metal                                  |
| <b>PTFE</b>  | Polytetrafluoro Ethylene                              |
| <b>RH</b>    | Relative Humidity                                     |
| <b>RHE</b>   | Reference Hydrogen Electrode                          |
| <b>SEM</b>   | Scanning Electron Microscopy                          |
| <b>SHE</b>   | Standard Hydrogen Electrode                           |
| <b>TEM</b>   | Transmission Electron Microscopy                      |
| <b>T-T</b>   | Takenaka-Torikai                                      |
| <b>VC</b>    | Vulcan XC72R                                          |
| <b>XRD</b>   | X-ray Diffraction                                     |
| <b>XRF</b>   | X-ray Fluorescence                                    |

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*Dedicated to both of my grandmothers, who went to be with the Lord  
when this thesis was written.  
Thank you for the love and care that you have given to me.*

# **Chapter 1: Introduction**

## **1.1 Global Energy Challenges in the 21<sup>st</sup> Century**

The rise of energy demand due to the increase in consumption and population over the last few decades has awakened the awareness of the possibility of a significant energy crisis in the future. Not only the sufficiency of the energy resources is at stake, but also the environmental effects caused by the usage of such a massive amount of energy is of great concern for many stakeholders.

A moderate forecast assumes that global energy consumption in 2050 will hit 27.6 TW or about twice as much as the 2001 consumption [1]. Although fossil fuel resources, particularly coal, could meet this demand, the CO<sub>2</sub> emitted by such an amount of coal consumption will shift the balance of the CO<sub>2</sub> cycle on earth. The utilization of conversion devices with a higher efficiency along with the substitution of the non-sustainable fossil fuels with more sustainable fuels are important ways to lower CO<sub>2</sub> emissions, i.e., to keep the CO<sub>2</sub> level in the atmospheric at its equilibrium level. The rise of CO<sub>2</sub> levels especially in densely populated areas such as cities will likely to cause health and geopolitical issues.

## **1.2 Transportation Sector and Local Pollution Issues**

Transportation is a primary need in today's world and contributes significantly to our energy demand. According to the US Energy Information Administration (EIA) in 2018, ~29% of total US energy consumption (~97.4 quadrillions BTU) was contributed by the transportation sector. Of the total US energy transportation sector energy used, ~ 92% was still contributed by non-sustainable petroleum fuels (54% from gasoline, 23% from diesel, 12% from jet fuel, and



3% others) [2]. The report also reveals that the transportation sector in the US contributes to 68 metric ton CO<sub>2</sub> per billion BTU, topping the list of CO<sub>2</sub> emissions per unit energy in 2018. In the US, total CO<sub>2</sub> emissions contributed by the transportation sector is ~29% of the total of 5.3 million metric tons of CO<sub>2</sub> emitted in 2018, higher than in the industrial and power generation sectors [3]. Global analysis of the contribution of the transportation sector has been very similar. The transportation sector contributes to ~27% of the worldwide final energy consumption and 25% of the global CO<sub>2</sub> emissions [4,5]. The massive amount of CO<sub>2</sub> released is primarily due to the dependency of the transportation sector on fossil fuel energy carriers. Unlike the stationary applications, such as industrial and residential, transportation sector does not have the flexibility of using a direct energy generator or converter (e.g., solar panel or wind turbine). Batteries have been considered as a promising energy storage alternative. However, the long recharging time with relatively short range achieved and low volumetric energy density hinder the widespread adoption of battery electric vehicles in the transportation sector, particularly for heavy duty vehicles [6]. Consequently, the development of renewable fuels dictates the pace of the transportation sector in the race towards sustainability in the near future. In fact, now the development of renewable fuels is relatively slow compared to that of renewable energy generators. A foreseeable continuous high reliance on fossil fuels in the transport sector globally could lead to some potential problems because of the negative environmental and health impacts, energy security, and geopolitical issues.

The importance of the transportation sector is not only because of its major contribution to the global CO<sub>2</sub> emissions, but also to the local air quality especially in densely populated areas. CO<sub>2</sub> and other pollutants (NO<sub>x</sub>, volatile organic compounds, particulate matter, etc.) from the transportation sector are concentrated in cities where most people live and work. Cities, due to

their limited green area, absorb and recycle these pollutants slowly yielding a higher lifetime of these harmful gases in atmosphere. Brandon and Kurban report that fossil fuel based vehicles are responsible for the pollution in many of the world's mega cities, which have caused millions of premature death in 2012 [7]. Similarly, Jacobson *et al.* claim that 3700 - 6400 lives can be saved annually by eliminating all current vehicles exhaust in the US [8]. This health benefit in reduction of CO<sub>2</sub> and other harmful pollutants in a densely populated area is most often overlooked. The improved health of a city also leads to a more productive society and promotes economic advantages in the longer-term by compensating the cost of illness treatment.

The more comprehensive view of the impact of global and local harmful pollutants from the transportation sector requires a more comprehensive solution. Given all of the considerations, the ideal fuel for the transportation sector is a non-carbon based fuel made with a zero carbon footprint, in which no CO<sub>2</sub> is produced either at the point of use or during production. The development and implementation of such fuels and their supporting infrastructure (from production to consumption) may need a long time and complicated development, while the immediate, do-able changes need to be implemented soon. The more realistic and immediate actions should focus on reducing the pollutants at the point of use from our vehicles. In other words, the implementation of non-hydrocarbon based fuels (such as hydrogen) as a transportation fuel or the application of battery electric vehicles could be a realistic shorter-term solution. With the development of hydrogen infrastructures and hydrogen-fed vehicles, local urban air quality can be significantly improved. A more localized production of hydrogen at the point of production also allows the possibility to implement a more established CO<sub>2</sub> recycle process such as carbon capture and storage (CCS) which may significantly reduce the amount of CO<sub>2</sub> being released to the air.

In this scenario, the conversion from internal combustion engine vehicles (ICEVs) into electric vehicles, both battery electric vehicles (BEVs) and fuel cell electric vehicles (FCEVs) is critical. Although converting over one billion ICEVs seems to be a nearly impossible projection, the progress shown has been promising. Now, we have over 5 million of EVs on the road (including ~30% hybrid) and the number keeps increasing due to the progress in technology development and economical and political incentives from the stakeholders [9]. Innovations to further make BEVs and FCEVs more competitive and surpass their counterpart ICEVs are the main challenges to be done.

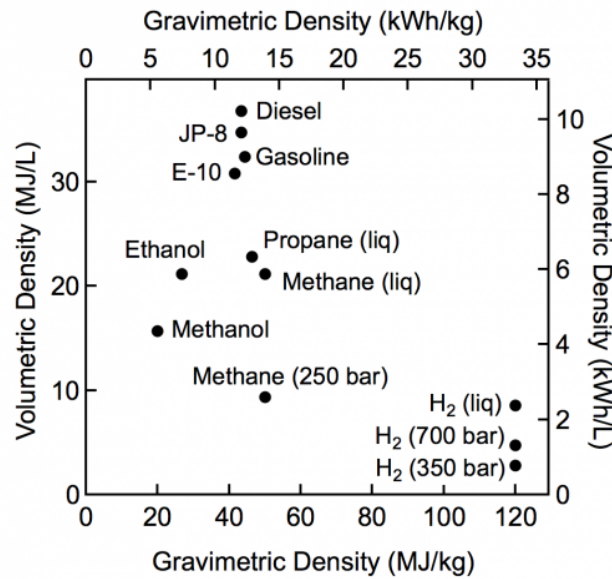
### **1.2.1 Transportation Fuels**

Fuel is a source of energy in a vehicle. The amount of potential energy in a fuel is characterized by a variable called heating value. There are two types of heating values that are commonly used: high heating value (HHV) and low heating value (LHV). They both are defined as the amount of energy heat released by combusting a specified quantity of fuel. The difference between HHV and LHV is that the former takes into account the latent heat of vaporization of water, whereas the later does not. Heating value of a fuel is generally represented by a thermodynamic term enthalpy of combustion ( $\Delta H_{\text{combustion}}$ ) and can be expressed as energy per mole or energy per mass density. Table 1.1 shows that fuels in the gaseous phase such as hydrogen and methane have a lower heating value per mole, but higher specific energy (heating value per mass) due to their low molecular weight. For the application in automotive sector, it is highly desirable for the fuel to be lightweight to reduce the energy needed to run the vehicle. Therefore, the application of gaseous fuels is promising in this regard. On the other hand, the limitation of space and complexity of fuel storage in a vehicle requires the gaseous fuels to be

compressed or even liquefied for automotive applications. As indicated by Table 1.1 and Figure 1.1, the volumetric energy density, i.e., energy content per volume, increases significantly by compression or liquefaction, which allows more energy to be stored within a limited space in a vehicle. The volumetric energy density of hydrogen, for example, increases significantly from  $12.8 \text{ MJ m}^{-3}$  under ambient pressure (gaseous state) to  $\sim 5,000 \text{ MJ m}^{-3}$  at 700 bar compression, and  $\sim 10,000 \text{ MJ m}^{-3}$  after liquefaction.

**Table 1.1. Several transportation fuels and their heating values [10]**

| Fuel     | Phase  | High Heating Value      |                        |                       |
|----------|--------|-------------------------|------------------------|-----------------------|
|          |        | (kJ mol <sup>-1</sup> ) | (MJ kg <sup>-1</sup> ) | (MJ m <sup>-3</sup> ) |
| Gasoline | liquid | 5,013                   | 46.4                   | 34,613                |
| Diesel   | liquid | 10,219                  | 45.6                   | 38,552                |
| Methanol | liquid | 726.0                   | 23.0                   | 18,200                |
| Hydrogen | liquid | 285.8                   | 141.8                  | 10,027                |
| Hydrogen | gas    | 285.8                   | 141.8                  | 12.8                  |
| Methane  | gas    | 890.3                   | 55.5                   | 37.7                  |



**Figure 1.1: Comparison of gravimetric and volumetric energy density of various transportation fuel**

[11]

### **1.2.2 Power and Energy for Automotive Applications**

In addition to the high energy content supplied by the fuel used, a conversion device that can produce high power is also critical. The simplified Ragone plot in Figure 1.2 shows a number of energy storage and conversion devices with their specific power and energy values [12]. The specific energy of the fuel cell is equivalent to the combustion engine of the conventional vehicle given the high energy content per mass of the hydrogen (or other alternative fuels). However, the combustion engine has higher power than fuel cells as a result of combustion mechanism that produces high amount of energy in a relatively short period of time (power = energy per time). On the other hand, fuel cells, which use electrochemical reactions, undergo a slower reaction rate as a result of several limitations or losses that will be discussed in subsequent sections. Despite the lower specific power compared to the internal combustion engine, fuel cells with their electrochemical reaction mechanism yield a significantly higher chemical to electricity energy conversion, which offers economic and technical benefits for the automotive application. The higher conversion efficiency of fuel cells has become one of the main reasons for the increasing trend to use this technology. The application of fuel cell for heavy duty vehicles such as trains, buses, trucks and ships, in particular, has gain considerable interest lately. The characteristics of hydrogen fuel cells with shorter charging time, longer range operation, higher energy density, and better durability than batteries have rendered the fuel cell to dominate heavy duty vehicle applications.

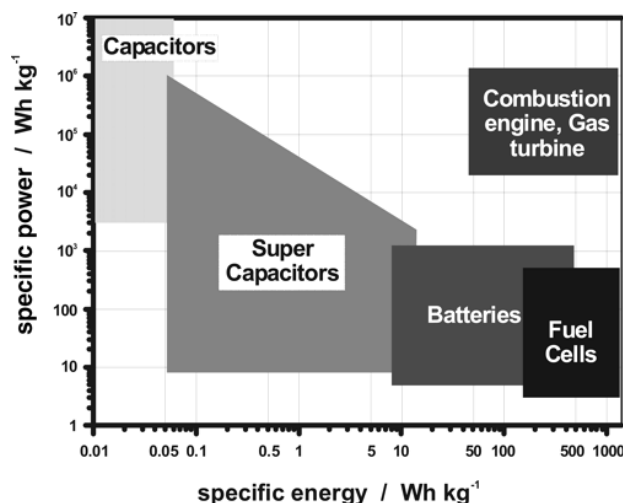


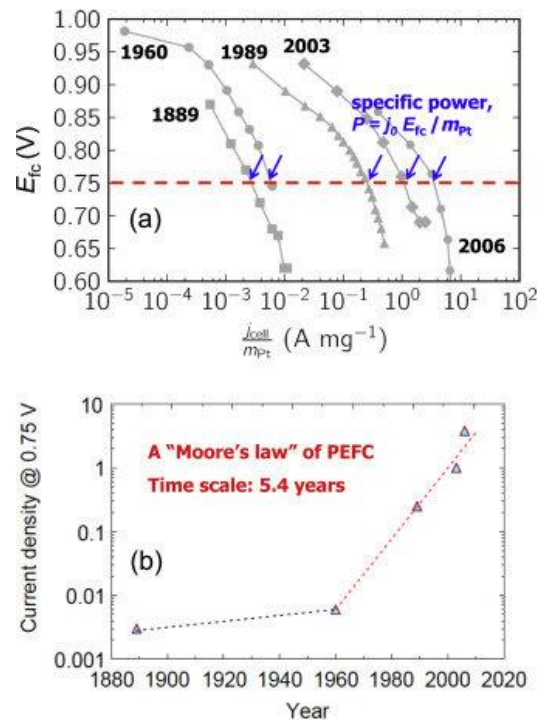
Figure 1.2: Ragone plot of various electrochemical devices compared to the internal combustion engine. Reprinted from Winter et al [12] with permission from ACS.

### 1.3 Historic Overview and Development of PEM Fuel Cell

The genesis of fuel cell started in 1838 when a German-Swiss scientist, Christian Schöenbein, made his discovery and published a paper on the interaction between hydrogen and oxygen molecules. At the same time a British physicist, William Grove, also worked and published an article on a sulfuric acid-based hydrogen-oxygen conversion device. Grove called this fuel cell ancestor device a “gas voltaic battery”. A year later, the first fuel cell patent was issued by the US patent office on an improved Grove cell with porous platinized coke as electrodes [13]. In 1889, the term fuel cell was first coined by Charles Langer and Ludwig Mond, who work on the first coal-based fuel cell. Up until the 1950s, fuel cell research had been limited only in research scale or restricted to small size cells, which could only deliver a small amount of current. The first recorded fuel cell system demonstration happened in 1959 when Francis Bacon first demonstrated his 5 kW alkaline fuel cell at a current density of  $700 \text{ mA cm}^{-2}$  at Cambridge University [13]. In the same year, the first patent on solid polymer electrolyte was issued by Willard Grubb from General Electric (GE), which at that time heavily researched fuel

cells, particularly those with polymer electrolyte. GE then developed Gemini space program with NASA to use fuel cell for space missions in 1960s [14].

General Motors and Shell came into the game in the mid 1960 with a focus on hydrogen and direct methanol fuel cells for vehicle applications. Ballard Power System, a company located in British Columbia, followed their steps and became the first company to predominantly focus on polymer electrolyte fuel cell research and development for several different types of applications. In the 1990s the application of Nafion as an electrode separator led to a new era of fuel cell technology. The research and development intensified leading to the commercialization of the hydrogen polymer electrolyte fuel cell leaving the other types of fuel cell behind.



**Figure 1.3: Highlights of polarization curves of fuel cells based on the milestones over the last 125 years. (Reprinted from Eikerling et al [14] with permission from CRC Press)**

The first demonstrated fuel cell in 1889 by Mond and Langer utilized thin porous leaves of Pt covered with Pt black particles of 0.1 mm size as the catalyst and a porous ceramic material

soaked in sulfuric acid as the electrolyte. With this structure, a Pt loading of  $2 \text{ mg cm}^{-2}$  produced only  $20 \text{ mA cm}^{-2}$  at a potential of  $0.6 \text{ V}$  [15]. The application of a proton conductive membrane as a separator in the early 1960s marked a new era in fuel cell history as indicated in Figure 1.3. In the cell designed by Grubb and Niedrach in 1960, a sulfonated cross linked polystyrene polymer was used, and the performance gain over the previous type was evident [16]. Despite the increase in mass activity shown, the proton conductivity of this membrane was low and the lifetime was short. This first generation of PEMFC was used for the famous NASA Gemini space program. A typical stack used consisted of 96 cells producing a total of  $1 \text{ kW}$  electricity ( $38 \text{ mW cm}^{-2}$  at  $0.83 \text{ V}$ ) [13]. From the overview of the history of fuel cell, it is clear that the performance leaps were always associated with a structural change or the invention of a new, breakthrough material. With the current challenge to further lower the catalyst loading significantly, the fuel cell community needs to explore the possibility of modifying the conventional fuel cell structure or inventing new fuel cell component materials.

## **1.4 Hydrogen PEM Fuel Cells**

Of all the fuel cell types, the hydrogen proton exchange membrane (PEM) fuel cell is considered as the most suitable fuel cell for the automotive applications. The hydrogen PEMFC also tops the list in terms of commercialization stage and research development owing to its high-power density and low-temperature operation features.

### **1.4.1 Hydrogen PEMFC Structure**

In a hydrogen PEM fuel cell (Figure 1.4), hydrogen is fed to the anode catalyst layer (ACL) passing through a series of layers consisted of a conductive flow field, a fibrous carbon



layer called the gas diffusion layer (GDL), and a microporous layer (MPL). Equation (1.1) shows the dissociation or oxidation reaction of hydrogen occurs in the ACL and its standard redox potential:



The protons then travel through a proton exchange membrane to reach the cathode side, while the electrons are collected through an external current collector. Oxygen travels from the cathode flow field plate to the cathode catalyst layer (CCL) through a GDL and an MPL and reacts with protons from the proton exchange membrane to produce water. Equation (1.2) shows the oxygen reduction reaction at the cathode catalyst layer:

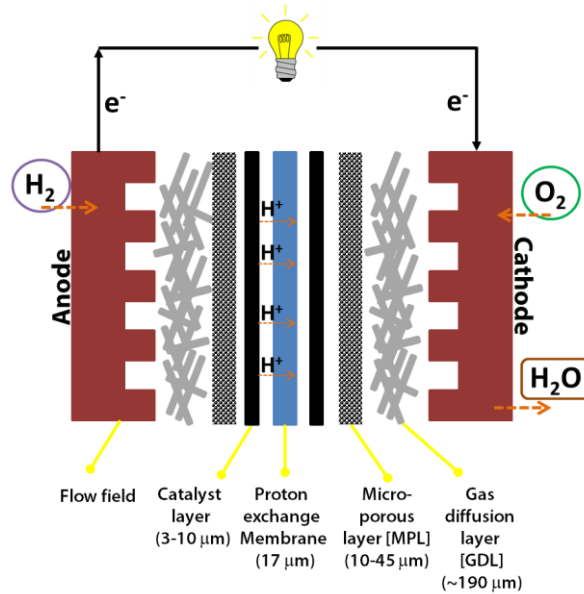


The overall hydrogen PEMFC reaction is from the combination of Equations (1.1) and (1.2):



The GDL is a layer (~200  $\mu\text{m}$  thick) consisting of carbon fiber or cloth with a hydrophobic agent mixture to prevent flooding. The fibrous or cloth structure provides the mechanical strength needed and distributes the gas evenly across the surface of the CL. The MPL is also a hydrophobic carbon-based layer (less porous than GDL) that is situated in between the GDL and the catalyst layer and has multiple important functions. The roles of the MPL will be described in detail in the subsequent sections. The anode and cathode catalyst layers consist of carbon supported platinum nanoparticles (typically 2-3 nm) with a mixture of liquid ionomer to improve proton conductivity. The Pt loading of the ACL (~0.04 - 0.1  $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$ ) is typically one order of magnitude lower than the CCL (~0.1 – 0.4  $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$ ) due to the different kinetic activity of Pt

towards hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). The exchange current density values for HOR on Pt surface ( $\sim 10^{-3} \text{ A cm}^{-2}_{\text{Pt}}$ ) are around six orders of magnitude lower than for the ORR ( $\sim 1 - 3 \times 10^{-9} \text{ A cm}^{-2}_{\text{Pt}}$ ). A thin ( $<100 \text{ }\mu\text{m}$ ) proton exchange membrane with high proton conductivity and mechanical strength is located at the center of this multi-layer architecture to transfer protons from the anode to the cathode and prevent electrons and reactants from crossing to the other side. This multi-layer architecture is widely known as the membrane electrode assembly (MEA), which is the heart of the PEMFC.



**Figure 1.4: Schematic of a PEMFC and its components**

## 1.4.2 Fuel Cell Thermodynamics

Given the standard-state reversible potential of the hydrogen PEMFC ( $E^{\circ}_{\text{cell}}$ ), one can find the standard-state molar free energy change ( $\Delta\hat{g}^0$ ) as follows<sup>1</sup>:

---

<sup>1</sup> Gibbs free energy ( $G$ ) is thermodynamically defined as the maximum energy that can be extracted from a system (unit: J). In other words,  $G$  represents the work potential of a system. Mathematically, one can write Gibbs free energy as  $G = H - TS$ . Gibbs free energy per mole of gas basis is represented by  $\hat{g}$  (unit:  $\text{J mol}^{-1}$ )

$$\Delta\hat{g}^{\circ} = -nFE^{\circ} \quad (1.4)$$

where  $F$  is the faraday constant ( $96,485 \text{ C mol}^{-1}$ ) and  $n$  denotes the number of moles involved.

The correlation between  $\Delta\hat{g}$  and the cell potential  $E$  is also useful to determine the effects of temperature and reactant concentration on cell potential under non-standard conditions.

Considering the definition of molar entropy ( $\Delta\hat{s}$ ) at constant pressure:

$$\left(\frac{d(\Delta\hat{g})}{dT}\right)_p = \Delta\hat{s} \quad (1.5)$$

The equation can be rearranged into:

$$\frac{d(E)}{dT} = \frac{\Delta\hat{s}}{nF} \quad (1.6)$$

Assuming  $\Delta\hat{s}$  is independent of temperature, at constant pressure, the effect of temperature ( $T$ ) to the reversible cell potential can be calculated by:

$$E_T = E^{\circ} + \frac{\Delta\hat{s}}{nF}(T - T_0) \quad (1.7)$$

where  $T_0 = 298.15 \text{ K}$ ,  $E^{\circ}$  is standard reversible cell potential, and  $E_T$  is reversible cell potential at temperature  $T$ .

Chemical potential is a measurement of how much the Gibbs free energy changes as the chemistry of the system changes. When temperature, pressure, and all other species are constant, chemical potential of species  $i$  is expressed as:

$$\mu_i = \left(\frac{dG}{dn_i}\right)_{T,P} \quad (1.8)$$

where  $dG/dn_i$  indicates how much the Gibbs free energy of the system changes for an infinitesimal increase in the quantity of species  $i$ . The effect of concentration to cell potential is derived from the chemical potential ( $\mu$ ) and activity ( $a$ ) relationship:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (1.9)$$

where  $\mu^0$  is the reference chemical potential at standard state conditions and  $a$  is the activity of species  $i$ . Given the equations (1.8) and (1.9), changes in Gibbs free energy can be calculated by:

$$dG = \sum_i (\mu_i^0 + RT \ln a_i) dn_i \quad (1.10)$$

For a reaction with a number of reactants and products, Equation (1.10) can be expanded into:

$$\Delta \hat{g} = \Delta \hat{g}^0 - RT \ln \frac{\sum_j \lambda_p a_{\text{prod},j}}{\sum_j \lambda_r a_{\text{react},j}} \quad (1.11)$$

Therefore, the reversible cell potential can be described as follows:

$$E = E^0 - \frac{RT}{nF} \ln \frac{\sum_j \lambda_p a_{\text{prod},j}}{\sum_j \lambda_r a_{\text{react},j}} \quad (1.12)$$

In the case of the hydrogen PEMFC, the activities of the gases is approximately equivalent to their partial pressure and the activity of liquid water is approximated as unity.

The theoretical efficiency ( $\eta$ ) of the fuel cell is calculated by taking a ratio between Gibbs free energy (maximum possible energy output) and the enthalpy of the fuel (i.e, energy input).

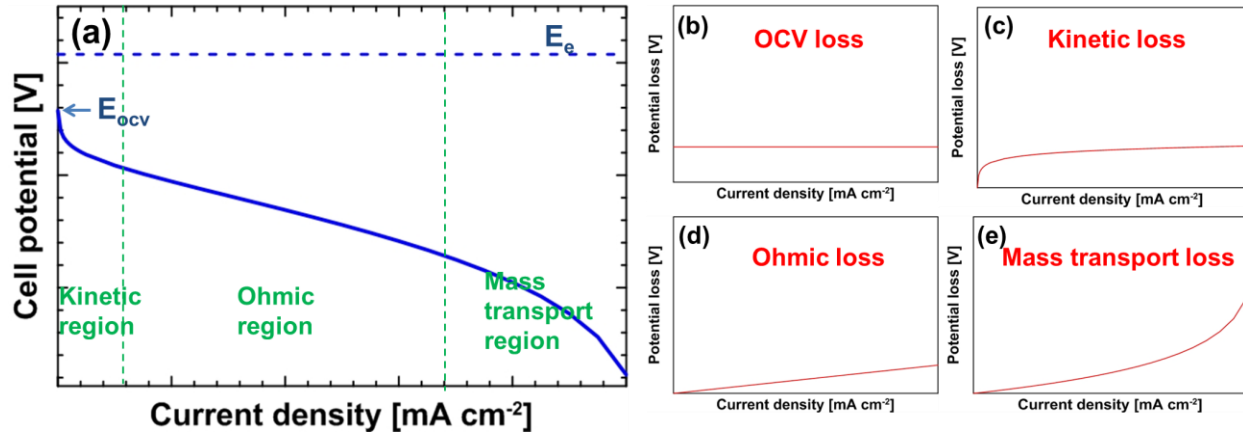
$$\eta = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (1.13)$$

where  $\Delta G$  is Gibbs free energy,  $\Delta H$  is the enthalpy, and  $\Delta S$  is the entropy of the system.

### 1.4.3 Polarization or Performance Losses

Electrochemical polarization is an in-situ electrochemical measurement of a fuel cell MEA that characterizes the correlation between cell potential (V) and cell current density (i). The polarization curve is useful to provide an overall quantitative evaluation of fuel cell maximum

power density and losses associated with fuel cell performance. As depicted in Figure 1.5, there are four fuel cell performance losses causing the drop in fuel cell performance: OCV, kinetic, ohmic, and mass transport loss. All individual performance losses will be discussed in the following sub-chapters.



**Figure 1.5: (a) Example of a polarization curve and its potential drop from the ideal equilibrium potential ( $E_e$ ) due to four performance losses: OCV, kinetic, ohmic, and mass transport loss (b-e).**

#### 1.4.3.1 OCV Loss

OCV loss is a potential loss that occurs at zero current due to the reactant crossover and parasitic reactions. The OCV loss causes the cell potential at open circuit ( $V_c^{OCV,m}$ ) to drop by typically 0.15 - 0.25 V from the equilibrium potential ( $V_c^{OCV,t}$ ). In hydrogen PEM fuel cells, hydrogen molecules permeate through the pores of the membrane and recombine with oxygen on the other side. The permeation of  $H_2$  through the membrane is referred to as hydrogen crossover, which lowers the cell potential at open circuit condition and the quantity of hydrogen crossing to the cathode determines the OCV loss due to hydrogen crossover. Another factor that contributes significantly to the OCV loss in hydrogen PEM fuel cells is the mixed potential due to the formation of Pt oxides at the Pt electrode. A mixed potential is the steady state potential of an open system that is lower than the thermodynamic potential. In a hydrogen PEMFC system, the

thermodynamic potential is determined by the four electron reduction of the oxygen reduction reaction ( $V_c^{OCV,t} = 1.23$  V). However, the occurrence of the side reactions at the cathode such as the reaction of Pt and water in an acidic medium ( $Pt + H_2O \rightarrow PtO + 2H^+ + 2e^-$ ;  $V_c^{OCV,t} = 0.88$  V) can contribute to the overpotential which lowers the OCV [17].

#### 1.4.3.2 Kinetic Loss

In electrochemical reactions, the reaction rate is represented by current (I in mA) or current density (i in mA cm<sup>-2</sup>). Like the reaction rate in chemical reactions, current density in electrochemical reactions obeys the Arrhenius law. In other words, current density is exponentially dependent on the activation energy ( $E_a$ ). The size of the activation energy in electrochemical reactions can be manipulated by sacrificing available potential and thus accelerate reaction rates. The conversion between cell potential and current density of a reaction is governed by the widely known Butler-Volmer equation:

$$i = i_0 \left( e^{\frac{\alpha n F \eta_{kinetic}}{RT}} - e^{\frac{(1-\alpha) n F \eta_{kinetic}}{RT}} \right) \quad (1.14)$$

where  $\eta_{kinetic}$  is the kinetic potential loss or overpotential,  $\alpha$  is the transfer coefficient that depends on the symmetry of the activation barrier, and  $i_0$  is the exchange current density. In cases where the overpotential is high (greater than 50-100 mV at room temperature), the Butler-Volmer equation can be simplified into the Tafel equation:

$$i = i_0 e^{\frac{\alpha n F \eta_{kinetic}}{RT}} \quad (1.15)$$

$$\eta_{kinetic} = -\frac{RT}{\alpha n F} \ln i_0 + \frac{RT}{\alpha n F} \ln i \quad (1.16)$$

#### 1.4.3.3 Ohmic Loss

The ohmic loss ( $\eta_{\text{ohmic}}$ ) accounts for the potential loss caused by the ionic and electronic resistances of all MEA components as well as the interfaces. The primary contributor of the ohmic loss is the ionic resistance of the membrane. The ohmic loss increases linearly with current density as indicated by the ohmic law ( $\Delta V = I \cdot \Delta R_{\text{ohmic}}$ ). This linear relationship can be clearly observed in the middle region of a polarization curve where the effects of kinetic and mass transport losses are at a minimum.

#### 1.4.3.4 Mass Transport Loss

Mass transport (MT) loss accounts for the potential loss caused by the starvation of reactants at the catalytic sites. The electrochemically reactive sites (also known as triple phase boundaries) are sites where protons, oxygen, and electronically connected catalyst contact. When one or more of these reactants are unable to reach the active catalytic sites, the catalytic sites become inactive. It consequently reduces the overall potential, which corresponds to the mass transport losses. Generally, owing to the electronically conductive properties of the GDL, MPL, and catalyst layer, an MEA suffers from mass transport losses mainly due to proton and oxygen depletion. Certain conditions for instance high current density operation will intensify reactant consumption and hence show a more pronounced effect of mass transport. The reactant depletion affects two variables of fuel cell performance: Nernstian losses and reaction losses. These two losses yield the mass transport loss. The mass transport loss depends on how much reactant and product concentrations differ from their bulk concentrations ( $C_{r,b} - C_{r,s}$ ). The current at which the reactant concentration falls to zero is referred to as the limiting current density ( $i_L$ ).

$$i_L = nFD^{\text{eff}} \frac{C_{r,b}}{\delta} \quad 1.17$$

The overpotential caused by mass transport loss is described as:

$$\eta_{\text{MT}} = \left( \frac{RT}{nF} \right) \left( 1 + \frac{1}{\alpha} \right) \ln \frac{i_L}{i_L - i} \quad 1.18$$

#### 1.4.4 Operational Flexibility

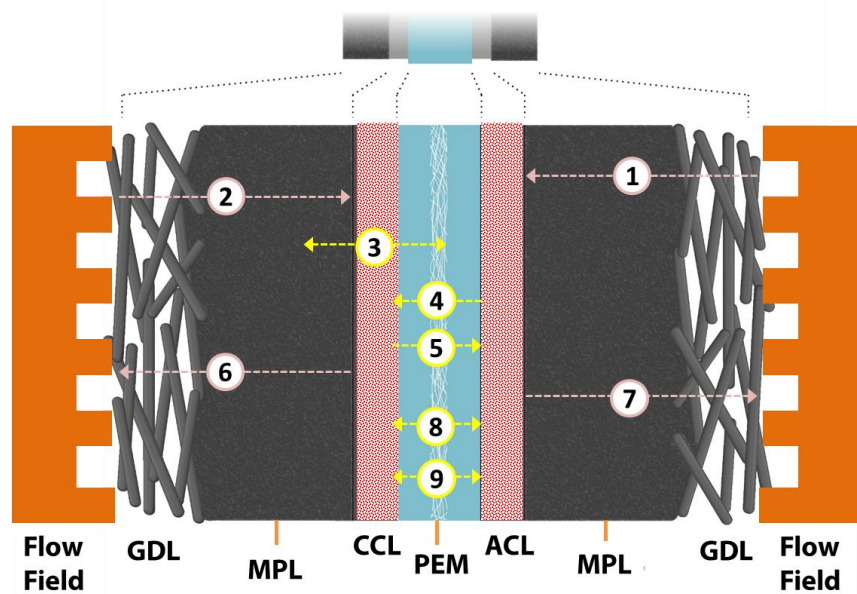
Automotive applications have been considered as the main driver for the commercialization of PEMFC technology. In order to bring this technology closer to full automotive fuel-cell commercialization, the improvement of fuel cell performance at different operational conditions is needed. The goal of improvement in operational flexibility is to minimize performance loss for different operational conditions particularly at low humidity (drying condition) and high current density conditions with lower catalyst loading catalyst layers.

##### 1.4.4.1 Water Management

Water, in liquid or vapor form, is a critical component in fuel cell operation. In PEMFC operation, water enters through humidified inlet streams of hydrogen and oxidant (arrows 1 and 2 in Figure 1.6). Water is also produced in the CCL from the ORR (arrow 3), which depends on the operational current density. Water can also move from one to another component of the MEA through different mechanisms (arrows 4-9). The electroosmotic drag force transports water with protons from the ACL to CCL through the membrane due to the potential gradients. Water can also move in the opposite direction (from the CCL to the ACL) due to concentration gradient, and the mechanism is called back-diffusion. Enhancement of water back-diffusion from CCL to ACL is considered as one of the most important factors to improve the overall performance.



During operation at high current densities, water is produced at higher rates at the cathode and needs to be removed to prevent flooding in the catalyst layer. Flooding in the CCL will block pathways available for air, which results in mass transport losses. Back-diffusion of water is also beneficial for low humidity operation as the water transported hydrates the membrane. Water movement indicated by arrows 8 and 9 are considered negligible when the anode and cathode of the cell are operated at the same temperature and pressure. All of the streams of water inside an MEA are described in Table 1.2. They constitute the water balance in PEMFC operation.



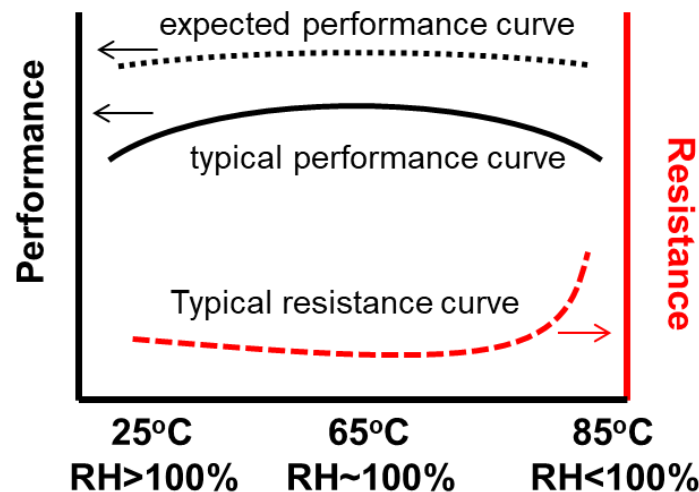
**Figure 1.6: Schematic of an MEA with water transport inside**

**Table 1.2. List of water movement inside an MEA during a PEMFC operation**

| Arrow | Water source/movement              | Driving force                 | Direction                             |
|-------|------------------------------------|-------------------------------|---------------------------------------|
| 1     | Water carried by hydrogen humidity | Relative humidity of hydrogen | Outside to anode                      |
| 2     | Water carried by oxidant humidity  | Relative humidity of oxygen   | Outside to cathode                    |
| 3     | Water produced by the ORR          | Operational current density   | Cathode to anode / cathode to outside |
| 4     | Electro-osmotic drag               | Proton transfer               | Anode to cathode                      |

|   |                                          |                          |                                     |
|---|------------------------------------------|--------------------------|-------------------------------------|
| 5 | Back-diffusion                           | Concentration difference | Cathode to anode                    |
| 6 | Water removal through cathode flow field | Convection, evaporation  | Cathode to outside                  |
| 7 | Water removal through anode flow field   | Convection, evaporation  | Anode to outside                    |
| 8 | Water moved via convection               | Gas pressure difference  | Anode to cathode / cathode to anode |
| 9 | Thermal osmotic drag                     | Temperature difference   | Anode to cathode / cathode to anode |

Under low humidity conditions, a PEMFC suffers from membrane dehydration which causes higher membrane resistance and lower proton conductivity [18]. On the other hand, at high humidity conditions, the membrane is susceptible to flooding due to excessive water produced in the cathode catalyst layer [19]. Water accumulation in the pores accelerates mass transport losses as it blocks more oxygen access to the catalyst layer. Zhang *et al.* show that the maximum power density of a PEMFC is reduced by ~80% when the reactant relative humidity decreases from 100% to 25% [20]. Generally, an external humidifier is used to maintain the humidity of the reactants resulting in higher costs and additional weight for the fuel cell system.

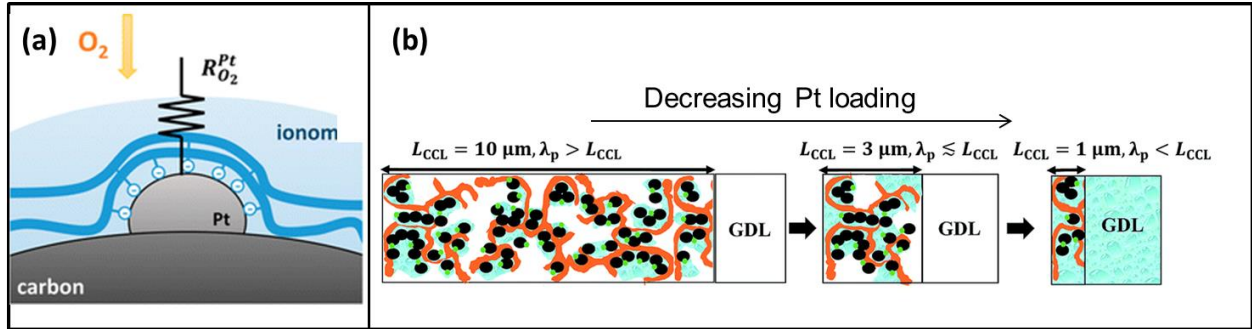


**Figure 1.7: Effect of humidity and temperature on the fuel cell performance (left y-axis) and resistance (right y-axis). The goal is to improve the performance at cold wet and hot dry condition (expected polarization curve).**

#### 1.4.4.2 Low Catalyst Loading Electrode

The recent trend to use lower precious metal or platinum group metal (PGM) content is inevitable to increase the competitiveness of the PEMFC compared to the internal combustion engine particularly in the automotive sector. The US DOE 2020 target of 0.125 mg<sub>PGM</sub> per cm<sup>2</sup> electrode (for total in both the anode and cathode electrodes) is a significant reduction from the commonly used 0.4 - 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> electrodes, and hence shows unexpected performance loss particularly at higher current densities. Studies have suspected two main causes of this increased mass transport loss at this level of loading, namely higher oxygen transport resistance through ionomer film surrounding catalyst, and more intense flooding due to a thinner catalyst layer. At lower loadings, an unknown resistance is identified after all the known resistances are removed suggesting the thin ionomer effect surrounding Pt catalyst as the most likely source of this loss [21]. This hypothesis is supported by an observation showing such losses are still present even when the catalyst layer is diluted with carbon [22]. Liu *et al.* add another insight and eliminate the possibility of unexpected resistance emerged from the thin ionomer coating in the catalyst layer. Based on their study, the resistance imposed by the ionomer does not scale up with thickness. This, therefore, results in the interfaces between Pt catalyst and the ionomer coating being the more likely source of the unexpected resistance [23]. A detailed study on the effect of non-Fickian oxygen transport resistance by Kongkanand and Mathias shows a linear relationship between the non-Fickian resistance relationship and the inverse of roughness factor ( $\text{ECSA} \times \text{Pt loading}$ ). Electrodes with low roughness factor show high non-Fickian resistance due to higher flux of oxygen delivered to a smaller Pt surface area [24]. The important finding in their study concludes that in the presence of Pt catalyst, the thin ionomer films lose their ability to segregate and hence form water and polymer domains. This leads to an attraction of sulfonic acid groups in

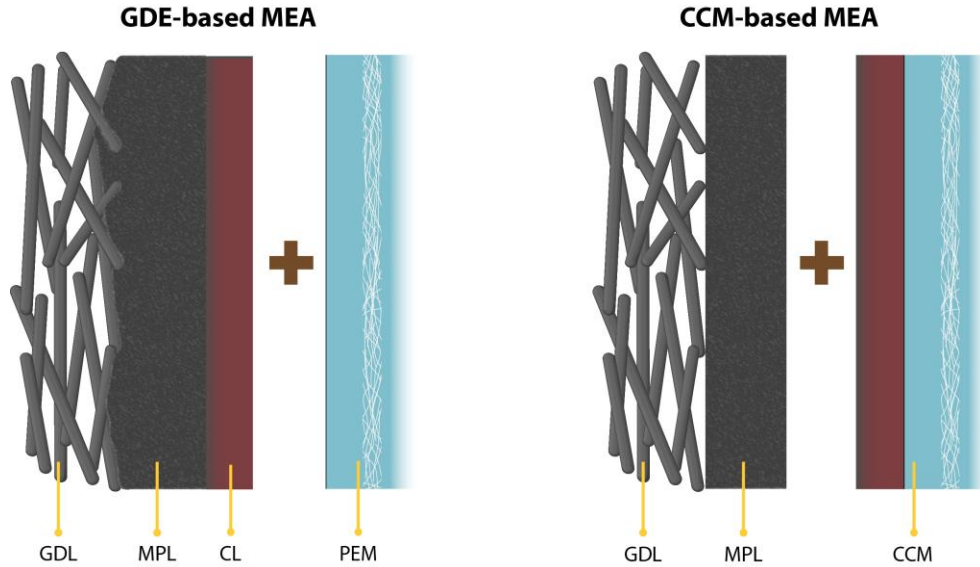
the ionomer by the Pt catalyst and causes a stiffer polymer backbone structure surrounding the Pt particle (Figure 1.8a). The stiffer backbone then increases O<sub>2</sub> and water transport in the Pt catalyst local area, and introduce the unknown mass transport resistance variable particularly at high current density operation, in which higher O<sub>2</sub> and water fluxes occur [24]. On the other hand, Muzzafar *et al.* conclude that it is the reduction of the catalyst layer thickness that causes the unexpected voltage losses with low cathode catalyst loadings. The thinner catalyst layers will lower the water vaporization capability and eventually diminish it when the layer is fully flooded (Figure 1.8b). Based on their modeling studies, the more realistic structure is Pt particles partially covered rather than fully encapsulated by an ionomer thin film. Under normal operation, Pt particles also surrounded by water, which acts as proton transport medium. The water surrounding Pt particles grow thicker as the flooding occurs and impedes oxygen diffusivity in the catalyst layer [25]. In summary, the two explanations agree on the increase of oxygen diffusivity in the surrounding of the catalyst layer as the main cause of the unexpectedly low performance of the MEAs with low cathode catalyst loadings at high current densities. The ionomer hypothesis emphasizes in the Pt-ionomer interaction to increase the oxygen diffusivity, while the water flooding hypothesis believes that the lower evaporation ability due to the thinner catalyst layer has caused the increase in mass transport losses. The former hypothesis suggests the improvement in ionomer structure to recover the performance, while the latter focuses on the MEA and catalyst layer structure modification to improve liquid water removal from the cathode catalyst layer.



**Figure 1.8: Schematics of the possible causes of the significant performance loss with a low Pt loading catalyst proposed in literature: (a) High oxygen resistance due to a stiffer polymer backbone as a result of polymer-Pt particle interaction, and (b) water accumulation due to reduced evaporation rate in a thinner catalyst layer. (Reprinted from Kongkanand et al [24] with permission from ACS Publications and from Muzaffar et al [25] with permission from RSC)**

## 1.5 MEA Components and Architecture

The membrane electrode assembly (MEA) can be fabricated by various methods (Figure 1.9). A catalyst layer, a microporous layer, and a gas diffusion layer stacked together make a single unit called the gas diffusion electrode (GDE). An MEA can be fabricated by combining a pair of GDEs and an ion exchange membrane in between. This assembly method is called GDE-based method. MEAs designed with this method will have a strong catalyst layer-MPL bonding, but consequently, it has a weaker membrane-catalyst layer bonding, which leads to an undesired kinetic performance losses [26,27]. The more widely use assembly method uses a symmetric structure comprised of an anode and a cathode catalyst layer coated on each surface of an ion exchange membrane, which is known as catalyst coated membrane (CCM). To complete the MEA, a CCM is pressed together with a pair of gas diffusion media layers. This assembly method results in a better connectivity between the membrane and the catalyst layers to improve the kinetic performance [28]. Interfacial gaps between the catalyst layers and the MPL on the cathode side, however, raise other transport problems that need to be addressed.



**Figure 1.9: Schematics of MEA assembled with GDE-based method (left) and CCM-based method (right)**

### 1.5.1 Ion Exchange Membrane

An electrochemical cell, with redox reaction occurring at both the anode and cathode, needs an electrolyte to transport charged ions between the electrodes. The electrolyte is a liquid, paste, or solid non-electronic conductive substance which can be made of a variety of chemicals. As discussed in Section 1.4, the development of the electrolyte is of paramount in the advancement of PEMFC performance. The evolution of fuel cell electrolyte materials started with liquid electrolyte (i.e., sulfuric acid) but achieved an important milestone when solid polymer first introduced in 1959. The type of solid polymer ion exchange membrane used has also been evolving from its original phenol sulfonic based polymers to the currently used perfluorosulfonic acid (PFSA) polymers like Nafion. The development over the last half a decade (1959 – present) has brought significant improvement in maximum power density achieved. The fuel cells with Nafion can achieve up to  $\sim 800 \text{ W ft}^{-2}$  or 80 fold higher than the first generation phenol sulfonic fuel cells ( $\sim 10 \text{ W ft}^{-2}$ ) [29].

PFSA-based membranes (e.g., Nafion) have a backbone structure similar to PTFE to provide the mechanical strength, but unlike PTFE, PFSA-based membranes also have sulfonic acid functional groups ( $\text{SO}_3^- \text{H}^+$ ). These sulfonic acid functional groups provide charge sites for proton transport and account for the proton conductivity of the polymer. The high stability and high ionic conductivity have resulted in the PFSA-based membrane as the most used electrolyte for PEMFCs. During operation, the membrane must be fully hydrated to maintain its conductivity. To prevent membrane dehydration due to evaporation and drying, operation at temperatures above 100°C or low humidity is not recommended.

Thinner PFSA-based membranes demonstrate an improved performance (i.e., lower resistance) at higher current density, especially at dry conditions where rehydration is needed [30]. Thinner membranes, however, are more prone to mechanical failure and have a higher rate of gas crossover which causes higher performance loss and degradation. Given the advantages of reducing the thickness, thinner membranes are preferred but the constraints need to be addressed. Membrane durability is also critical for maintaining fuel cell long-term performance. The membrane suffers from mechanical and chemical stability issues, which are accelerated under low humidification and high potential (such as OCV) operation. At OCV, in particular, the unreacted reactants can diffuse through the membrane result in run parasitic reactions. In the case of the hydrogen PEMFC, one of the main causes of membrane degradation is the formation of hydrogen peroxide in the membrane as a by-product [31].

### **1.5.2 Membrane | Catalyst Layer Interface**

The membrane | catalyst layer interface plays an important role in proton transfer from the membrane to the catalyst layer. Cheng *et al.* discover a significant loss in electrochemically

active surface area (ECSA) of a GDE-based MEA due to disconnection of proton transfer from the membrane to the catalyst layer. The claim that the proton deficiency is the main cause of the drop of the ECSA is supported by the recovery of ~77% of the ECSA after the enhancement of proton pathways to the electrode [26]. Leimin *et al.* also confirm the similar conclusion that the presence of the gaps between the membrane and catalyst layer leads to a higher charge transfer and ohmic resistances, which cause overall performance drop [32]. Tang *et al.* measured the gap under SEM and showed ~20  $\mu\text{m}$  gaps between the catalyst layer and membrane in a GDE-based MEA [27]. Such wide gaps between the catalyst layer and membrane could potentially lead to a lower membrane self-humidification ability as water produced from the ORR needs to travel across the gaps especially at low humidity operations.

#### **1.5.2.1 Pt Layer in Membrane Subsurface**

The deposition of platinum particles in the membrane subsurface is a way to enable water production in the vicinity of the membrane and therefore improves membrane self-humidification [33–36]. Sufficient protons, electrons, and oxygen molecules need to be supplied to the Pt particles for those particles to be active for ORR. The presence of deposited Pt particles in membrane subsurface can offer performance benefits especially for membrane electrode assemblies (MEAs) fabricated by combining of a pair of gas diffusion electrodes (GDEs) and a membrane, which result in an interfacial gap between the membrane and catalyst layer. Pt deposited in the membrane can also act as recombination sites and therefore suppress undesired hydrogen crossover from the anode to cathode during fuel cell operation [35]. This platinized membrane structure was first reported by Takenaka *et al.* for water electrolysis application in 1982 [37]. Takenaka *et al.* used a single step reaction of a metal salt solution (e.g.,  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ )



with a reducing agent (e.g.,  $\text{NaBH}_4$ ) to synthesis this structure, which is known as the Takenaka-Torikai (T-T) method. In 1990, the impregnation-reduction (I-R) method was introduced. The I-R method uses two separated steps by which the Nafion membrane is first ion-exchanged with Pt salt and then a reducing agent is used to reduce the impregnated Pt ions [38]. A further development of the I-R method, which stops the impregnation of Pt ions before reaching equilibrium, has yielded a shallower (submicron) deposition of Pt particles in the membrane subsurface and improved catalyst utilization due to improved reactant accessibility [39]. Table 1.3 summarizes a number of reported studies on optimization of synthesis methods and parameters in order to improve the functionality of the platinized membranes indicated by their performance metrics. Synthesis of platinized membrane for the membrane | CL interface targets a dense Pt layer at a membrane subsurface to minimize isolated Pt particles deeper in the membrane. Platinum particle interconnectivity is a critical parameter to achieve for this layer to improve the activity and functionality for membrane humidification.

Integration of metal and polymer structure, which is widely known as ionic polymer metal composite (IPMC), has been considered for a number of emerging applications such as: actuators [40,41], sensors [42,43], energy harvesters [44,45], and artificial muscles [46,47]. Platinized membrane structure, in particular, has been used for many electrochemical applications such as in low concentration hydrogen sensors [48,49], methanol electrolyzers [50], and fuel cell cathode catalyst layer structures [35,51–53]. For the last aforementioned application, the presence of the Pt layer in the membrane subsurface benefits the performance in many ways: i) improved membrane stability due to decomposition of harmful hydrogen peroxide [54], ii) membrane self-humidification, iii) suppression of hydrogen gas cross-over [35,36], and iv) improvement of operational flexibility.

**Table 1.3. Summary of the selected literature on electroless deposition of catalyst in membrane**

| Reference                        | Key Findings                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | Element/Loading                                                                                                                                                                   | Performance Metric                                                                                                                                                                                                               | Application                  |
|----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| Takenaka <i>et al</i> (1982)[37] | <ul style="list-style-type: none"> <li>First report of Takenaka-Torikai (T-T) one step method for metal deposition in Nafion 125 with deposition on both sides</li> <li>Exploration of surface roughening via O<sub>2</sub> plasma etching and hydrothermal pretreatment of the membrane</li> </ul>                                                                                                                                                                                                                                                | Ir, Rh, Pt, Pd, Rh-Pt, Ru-Pt:<br>1-2 and 3-6 mg/cm <sup>2</sup>                                                                                                                   | <i>OER overpotential:</i> Ir < Rh < Rh-Pt < Pt-Ru < Pt < Pd<br><i>Electrolysis cell:</i> Pt cathode, Ir anode, ~ 1.7 V @ 1000 mA/cm <sup>2</sup> , 90°C                                                                          | Water electrolysis           |
| Fedkiw <i>et al</i> (1989) [38]  | <ul style="list-style-type: none"> <li>First report of impregnation-reduction (I-R) two step method</li> <li>Cationic, neutral, and anionic reductants are tested, and the latter worked best</li> <li>ECSA and HOR activity are measured to determine optimum as a function of loading based on trade-offs between conductivity, particle size, and permeability</li> </ul>                                                                                                                                                                       | Pt : 2-6 mg/cm <sup>2</sup><br>Pd, Cu, Ni (unspecified loading)                                                                                                                   | <i>ECSA:</i> 5-14 m <sup>2</sup> /g<br><i>HOR:</i> 600 mA/cm <sup>2</sup> limiting current for 3.6 mg/cm <sup>2</sup> Pt                                                                                                         | Hydrogen oxidation           |
| Millet <i>et al</i> (1989) [55]  | <ul style="list-style-type: none"> <li>Deposition of Pt in Nafion 117 using I-R method</li> <li>Extensive electron microprobe concentration profiles across membrane for Pt, Ir, and/or Na<sup>+</sup> as a function of reductant concentration, number of precipitation cycles</li> </ul>                                                                                                                                                                                                                                                         | Pt: 1.13 mg/cm <sup>2</sup> (optimized parameters)                                                                                                                                | <i>Particle size:</i> 5-9 nm<br><i>Electrolysis cell:</i> 1.13 mg/cm <sup>2</sup> Pt cathode, 1.13 mg/cm <sup>2</sup> Pt + 0.2 mg/cm <sup>2</sup> Ir anode, ~ 1.75 V @ 1000 mA/cm <sup>2</sup> , 80°C                            | Electrolysis                 |
| Fedkiw <i>et al</i> (1990) [56]  | <ul style="list-style-type: none"> <li>Effect of [chloroplatinic acid] and [hydrazine] during deposition of Pt using T-T method in sanded Nafion 117</li> <li>Lower [platinum salt] leads to less compact, porous deposit while higher concentration yields dense film, but the deposition rate is unchanged</li> <li>Deposition rate is linearly proportional to [reductant]</li> <li>Slower deposition with anionic borohydride vs. hydrazine</li> </ul>                                                                                         | Pt: 3.1, 3.2, 7.0, 10.7 mg/cm <sup>2</sup>                                                                                                                                        | <i>Surface area:</i> 6 – 50 m <sup>2</sup> /g (gas in contact with Pt/Nafion), 7-55 m <sup>2</sup> /g (electrolyte in contact with Pt/Nafion)                                                                                    | Electroreduction of ethylene |
| Liu <i>et al</i> (1992) [39]     | <ul style="list-style-type: none"> <li>Comparison of T-T, equilibrium I-R and non-equilibrium I-R methods</li> <li>In non-equilibrium method, impregnation step is not allowed to reach equilibrium (gradient of Pt species)</li> <li>Pt distribution is dependent on initial Pt(II) profile and [reductant]</li> <li>Non-equilibrium I-R results in shallower deposit with better utilization but most difficult to reproduce</li> <li>Controlled study of effect of impregnation time, reductant concentration, Pt salt concentration</li> </ul> | Pt: 0.55 mg/cm <sup>2</sup> (non-eq. I-R), 3.6 mg/cm <sup>2</sup> (eq. I-R), 4.1 mg/cm <sup>2</sup> (T-T) (optimized)<br>Pt @ 0.5-7 mg/cm <sup>2</sup> (total range, all methods) | <i>Surface area:</i> 34 m <sup>2</sup> /g (non-eq. I-R), 13 m <sup>2</sup> /g (eq. I-R), 7 m <sup>2</sup> /g (T-T)<br><i>Pt 'Utilization':</i> 800 mA/mg (non-eq. I-R), 160 mA/mg (eq. I-R), 110 mA/mg (T-T) at limiting current | Hydrogen oxidation           |

| Reference                                | Key Findings                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | Element/Loading                                                                           | Performance Metric                                                                                                                                                                                                                           | Application                                |
|------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|
| 1995, P. Millet <i>et al</i> (1995) [57] | <ul style="list-style-type: none"> <li>• Discussion of two types of limiting kinetics, diffusion in the boundary diffusion layer (L) or diffusion in the membrane (M) being rate-determining</li> <li>• Equations to represent each mechanism</li> <li>• Rate-determining mechanism switches from L to M when salt concentration or stirring regime increased</li> <li>• The diffusion coefficient of <math>[\text{Pt}(\text{NH}_3)_4]^{2+}</math> is <math>8.3 \times 10^{-6} \text{ cm}^2/\text{s}</math> and <math>5.2 \times 10^{-7} \text{ cm}^2/\text{s}</math> in aqueous solution and the membrane, respectively (also report <math>[\text{H}^+]</math> values)</li> </ul> | -                                                                                         | -                                                                                                                                                                                                                                            | Theoretical study of impregnation process  |
| Millet <i>et al</i> (1995) [58]          | <ul style="list-style-type: none"> <li>• Equations to represent the precipitation process</li> <li>• Comparison of the experimental results to theoretical predictions (e.g., loading per cycle, platinum concentration profile)</li> <li>• Effect of [reductant], number of cycles, and rate of chemical reaction</li> <li>• Diffusion coefficients for all species</li> <li>• Nine moles of <math>\text{NaBH}_4</math> are required to reduce four moles of Pt tetraamine, note <math>\text{NaBH}_4</math> decomposition rate</li> </ul>                                                                                                                                         | Pt: 0.5-2.0 $\text{mg}/\text{cm}^2$                                                       | -                                                                                                                                                                                                                                            | Theoretical study of precipitation process |
| Watanabe <i>et al</i> (1998) [35]        | <ul style="list-style-type: none"> <li>• Use I-R method over long times (overnight) to deposit Pt in Nafion 112 (50 <math>\mu\text{m}</math>)</li> <li>• Resistance of platinized membrane MEA significantly lower due to 'self-humidification' effect</li> <li>• OCV higher as amount of crossover is reduced to only 1 <math>\text{mA}/\text{cm}^2</math> for platinized membrane MEA</li> </ul>                                                                                                                                                                                                                                                                                 | Pt: 0.09 $\text{mg}/\text{cm}^2$                                                          | Particle size: 1-2 nm (TEM)<br>Fuel cell: 0.37 $\text{mg}/\text{cm}^2$ Pt/C cathode and anode, 0.09 $\text{mg}/\text{cm}^2$ Pt in membrane, 0.55 V @ 1000 $\text{mA}/\text{cm}^2$ , 80°C (compared to 0.15 V for MEA without Pt in membrane) | Hydrogen fuel cell                         |
| Wang <i>et al</i> (2005)[34]             | <ul style="list-style-type: none"> <li>• Use I-R method to deposit Pt in custom PFSA membrane then combine with 0.3 <math>\text{mg}/\text{cm}^2</math> standard Pt/C layers</li> <li>• External humidification still shows better performance than self-humidification but the MEA with Pt in the PFSA membrane exhibits better performance than the MEA without</li> <li>• Three steps to self-humidification are permeation of <math>\text{O}_2</math> and <math>\text{H}_2</math>, internal adsorption to Pt, and recombination</li> </ul>                                                                                                                                      | Pt: 0.02-0.06 $\text{mg}/\text{cm}^2$                                                     | Particle size: 6 nm (XRD)<br>Fuel cell: 0.675 V @ 1000 $\text{mA}/\text{cm}^2$ , 70°C (compared to 0.575 V for MEA without Pt in membrane)<br>*No gas humidification*                                                                        | Hydrogen fuel cell                         |
| Weissmann <i>et al</i> (2007) [59]       | <ul style="list-style-type: none"> <li>• Use T-T method to deposit Pt in Nafion 117 and ADP to compare cation vs. anion exchange membranes</li> <li>• T-T method will lead to higher Pt utilization than I-R method</li> <li>• Report Tafel slopes, exchange current densities, and resistances for ORR in Pt in Nafion 117 and ADP</li> </ul>                                                                                                                                                                                                                                                                                                                                     | Pt: 0.8-1.8 $\text{mg}/\text{cm}^2$ (Nafion 117)<br>Pt: 2.1 $\text{mg}/\text{cm}^2$ (ADP) | Particle size: 2-14 nm (TEM), 10-26 nm (electrochemistry)<br>Roughness factor: 121-521 (~ 25-40 $\text{m}^2/\text{g}$ )                                                                                                                      | Oxygen reduction                           |

| Reference                              | Key Findings                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Element/Loading                      | Performance Metric                                                                                                                                                                                                                                                          | Application        |
|----------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
| Pethaiah <i>et al</i> (2011) [60]      | <ul style="list-style-type: none"> <li>Use non-equilibrium I-R method to deposit Pt on both sides of Nafion 1135 (88.9 <math>\mu\text{m}</math>)</li> <li>Hot press electroless Pt to 0.25 <math>\text{mg}/\text{cm}^2</math> GDE prepared with commercial Pt/C</li> <li>Propose disconnected Pt in membrane acts as recombination site for permeated <math>\text{H}_2</math> and <math>\text{O}_2</math>, thus 'self-humidifying' membrane</li> <li>MEA with electroless Pt shows higher performance, especially at higher current, than conventional Pt/C MEA with same loading (0.5 <math>\text{mg}/\text{cm}^2</math> total Pt)</li> </ul>                                                            | Pt: 0.25 $\text{mg}/\text{cm}^2$     | <i>Particle size:</i> 5.2 nm (electroless Pt, XRD), 3 nm (Pt/C, XRD)<br><i>Fuel cell:</i> 0.25 $\text{mg}/\text{cm}^2$ $\text{Pt}_{\text{Electroless}}$ + 0.25 $\text{mg}/\text{cm}^2$ Pt/C cathode and anode, 0.65 V @ 1000 $\text{mA}/\text{cm}^2$ , 75°C, 50 h stability | Hydrogen fuel cell |
| Sode <i>et al</i> (2011) [61]          | <ul style="list-style-type: none"> <li>Use I-R method to deposit Pt in Nafion 117, explore effect of <math>\text{K}_2\text{SO}_4</math> solution pH and membrane hydration pre-treatment on depth of deposition and deposit morphology</li> <li>Measure Pt in <math>\text{K}_2\text{SO}_4</math> solution after first step, supporting hypothesis Pt-amine is highly mobile in Nafion</li> <li>Propose that lower hydration level may inhibit <math>\text{BH}_4^-</math> (alone or as co-ion) transport, leading to shallow (200 nm) deposit compared to wet membrane (15 <math>\mu\text{m}</math>)</li> <li>Absorbed current image vs. SEM image comparison suggests 30% of Pt is unconnected</li> </ul> | Pt: 0.45 $\text{mg}/\text{cm}^2$     | <i>Surface area:</i> 7 $\text{m}^2/\text{g}$ (Au contact)                                                                                                                                                                                                                   | Analytical study   |
| Ingle <i>et al</i> (2014) [62]         | <ul style="list-style-type: none"> <li>Use I-R method to deposit in Nafion 117 and 112 to create low density Pt NP in Nafion 117 (10 <math>\mu\text{m}</math> region, Pt particles and nanowires) and surface localized high density of Pt NP in Nafion 112 (Pt polyhedrons and nanowires)</li> <li>Particle size and number density distribution different for two types of deposits</li> </ul>                                                                                                                                                                                                                                                                                                          | -                                    | <i>Particle size:</i> 5-10 & 40-50 nm (Nafion 117)<br><i>Particle size:</i> 2-20 nm (Nafion 112)                                                                                                                                                                            | Analytical study   |
| Martens <i>et al</i> (2016) [63]       | <ul style="list-style-type: none"> <li>Analysis of optical reflectivity and electronic conductivity of Pt thin film in Nafion and the effect of film morphology to those parameters</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Pt: 0.024 $\text{mg}/\text{cm}^2$    | <i>ECSA :</i> 15 $\text{m}^2/\text{g}$ , specific activity 0.48 $\text{mA}/\text{cm}^2\text{Pt}$ , mass activity 72 $\text{mA}/\text{mg}_{\text{Pt}}$                                                                                                                       | Analytical study   |
| Hosseiniabadi <i>et al</i> (2018) [64] | <ul style="list-style-type: none"> <li>Optimization of performance of Pt-coated Nafion by tuning synthesis conditions</li> <li>CCMs produced by ethylenediamine -modified Nafion show a higher ECSA and better fuel cell performance</li> <li>Increasing pH of <math>\text{NaBH}_4</math> reductant during synthesis further enhances ECSA and fuel cell performance</li> </ul>                                                                                                                                                                                                                                                                                                                           | Pt: ~0.1-0.3 $\text{mg}/\text{cm}^2$ | <i>ECSA :</i> 3-5 $\text{m}^2/\text{g}$<br><i>Fuel cell :</i> Electroless Pt + 0.2 $\text{mg}/\text{cm}^2$ Pt cathode and anode, max power : 412 $\text{mW}/\text{cm}^2$                                                                                                    | Hydrogen fuel cell |

### **1.5.3 Microporous Layer**

#### **1.5.3.1 Definition and Functions**

Microporous layer (MPL) is a transition layer with fine pore structures (low porosity) situated between the gas diffusion layer (GDL) and the catalyst layer (CL). In the conventional structure, an MPL is applied to the GDL and sintered at high temperature, i.e.,  $>200^{\circ}\text{C}$ , along with the GDL. Past studies have shown some benefits for the MPL in a PEMFC which include: (i) Improving the water homogeneity distribution in the cathode GDL (or localizing water entry locations into the GDL) [65–67]; (ii) acting as a pressure barrier for water diffusion in the cathode GDL and therefore forcing water back to the anode through the membrane [68–71]; (iii) breaking water molecules into smaller droplets and reducing liquid saturation [72,73]; (iv) increasing temperature in the electrode, which leads to a higher evaporation rate of liquid water [74–76], and (v) providing mechanical support and enhancing conductivity between layers [77,78].

#### **1.5.3.2 MPL Carbon Type**

Fine tuning of MPL variables such as carbon type, hydrophobic agent content, and thickness dictates the MPL properties, which plays an important factor in improving the MPL performance under specific conditions. Carbon black is the main constituent of an MPL due to its low price, high mechanical strength, high porosity, and high electronic conductivity. Vulcan XC-72R (VC), Acetylene Black (AB) and Black Pearl (BP) are still dominant as the most commonly used carbon black for the MPL due to their cheap price and high availability. In the conventional MPL structure, the effect of the MPL morphology on the performance has been studied. Jordan *et al.* show that an AB-based MPL achieves a 16% gain in maximum power density, both on  $\text{O}_2$

and air, vs. VC-based MPL [79]. Similarly, Antolini *et al.* demonstrated that the application of AB in the MPL results in a higher potential than VC at high current densities [80]. Chen and Chang also compare AB and BP-based MPL under humidified conditions and conclude that AB gives a better performance [81]. Simon *et al.* compare the effect of surface area by testing a smaller surface area AB ( $39 \text{ m}^2 \text{ g}^{-1}$ ) to the AB with  $\sim 68 \text{ m}^2 \text{ g}^{-1}$  surface area and show that a lower surface area AB reduces the oxygen transport resistance under over-humidified conditions at  $50^\circ\text{C}$  [82]. Recently, nanostructured materials such as carbon nanotube and nanofibrous carbon have also been introduced as MPL materials. Lin *et al.* show that a proper mixture of carbon nanotube and acetylene black improves MEA performance by balancing water saturation and reducing cell resistance [83]. Similarly, carbon nanofiber based MPLs demonstrate a better mechanical robustness and mass transport performance due to an improved gas permeability [29,84]. Carbon nanospheres exhibit lower degree of degradation and provide better conductivity. Other type of materials, e.g., Hicon black, paraffin wax carbon [85], pureblack nanocarbon chains [86], and electrochemically exfoliated graphene [87] have also positively impacted MEA performance compared to the typical Vulcan XC72R. Lately, composite MPL materials, such as graphene-carbon black and graphene-reduced graphene oxide have also been examined and show that this approach is useful to combine the merits from all individual MPL materials [88].

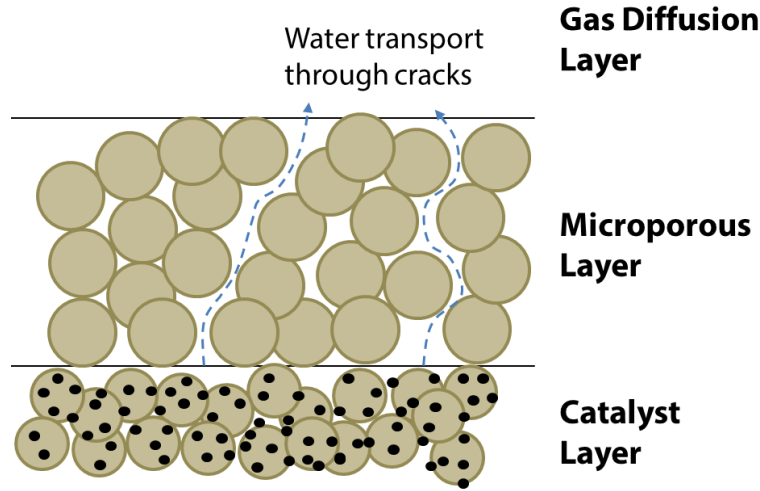
### 1.5.3.3 MPL Layer Properties and Thickness

In addition to the material properties, layer properties also play an important role for the MPL design. For most cases, MPL consisting of more hydrophobic pores are preferred than hydrophilic pores to enable more gas transport pathways through the pores and to lower water

saturation [89]. The hydrophobic pores have a higher capillary pressure to prevent liquid water from entering and residing within, and hence redirecting water flow via bigger pores or cracks as shown in Figure 1.10. These bigger pores or cracks for water transport can be purposely designed or result from natural defects occurred in the layer during synthesis. The smaller hydrophobic pores, therefore, function as a channel for gas transport from the GDL to the catalyst layer [90,91]. A higher capillary pressure also causes the water to back diffuse from the cathode to the anode through the membrane. A hydrophobic agent (e.g., PTFE) is typically mixed into the MPL to improve the hydrophobicity of the MPL, however, an excessive addition of the hydrophobic agent will enhance flooding as it reduces hydrophilic pathways needed for the water to escape [92]. An optimum content of 20% PTFE has been achieved with Vulcan carbon as an MPL material with 10 – 40% as an acceptable range [93–95]. Although a hydrophilic MPL shows no benefits under wet conditions, under dry (low humidity) conditions a hydrophilic MPL will act as a barrier to retard water evaporation and minimize resistance loss due to drying [70,96,97].

The MPL layer thickness also affects the overall performance in particular by changing water saturation at the CL|MPL interface. Antonacci *et al.*, for example, suggest that the liquid water volume at the CL|MPL interface decreases with thickness up to 50  $\mu\text{m}$  [98]. On the other hand, the cell potential in the higher current density region drops and the ohmic resistance increases at 60 °C and 100% RH conditions as the layer thickness grows beyond 50  $\mu\text{m}$ . The reason of this increase in ohmic resistance is a reduced back-diffusion to the anode by a thicker MPL. A thicker MPL acts as a greater thermal barrier to accelerate membrane dehydration [98]. Following up that work, Lee *et al* simulated water thickness level in a conventional MPL using synchrotron X-ray radiography and determined that the water content is higher in a thicker MPL

[99]. By doing computational work, Nanadegani *et al.* also discovered that a thicker layer could retain more water in the MPL and reduce the cell performance [89]. The characteristics of the ideal MPL has also been discussed thoroughly in Chapter 2.5 of reference [100].



**Figure 1.10: Schematic of the MPL and the layer crack or interparticle pore for liquid water transport**

#### 1.5.4 Catalyst Layer | Microporous Layer Interface

In order to optimize the benefits of having an MPL, an approach to modify the CL|MPL interface has been widely taken. The interface of the CL|MPL layers affects thermal conductivity, electrical conductivity and water-gas movement in the CL and MPL, and therefore plays an important role in PEMFC performance. Hizir *et al.* conducted a study to analyze interfacial surface morphology and observed that due to the rough and cracked nature of the MPL and CL, the interface between the two is imperfect. This may lead to a potential space for water storage, which benefits the performance at low current density. However, at higher current density the rate of water produced exceeds the storage capacity and causes flooding [101]. Utilizing the rapid freezing method, Tabe *et al.* confirmed this hypothesis that the larger gap between the CL and the subsequent diffusion medium layer (e.g., MPL) creates a water pool,



leading to reduced access of oxygen to the CL [102]. Another important modeling study done by Kalindini *et al.* also proposed a lower limiting current density with an imperfect CL|MPL compared to the interface without gaps [103]. Likewise, Zenyuk *et al.* observed that the CL|MPL interface with cracks on the surface of the MPL result in a higher water saturation due to its higher roughness, which results in a wider interfacial gaps compared to the non-cracked interface [104]. On the other hand, local ohmic, thermal and mass transport losses have also been studied, and show that those losses are increased upon the addition of an interface layer (compared to that with a perfect contact) [105]. A detailed literature survey on the CL|MPL interface is summarized in Table 1.4.

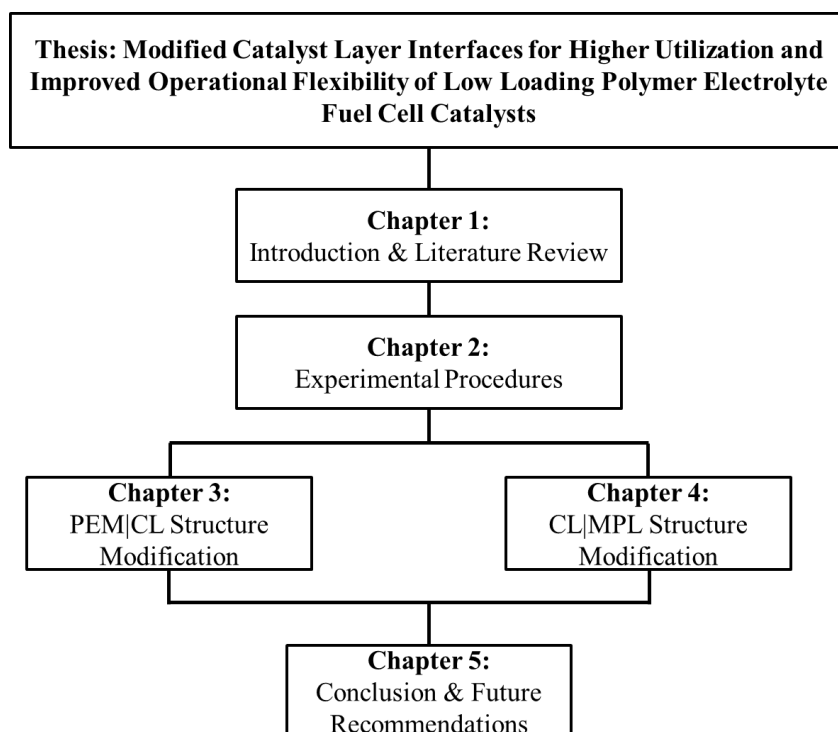
**Table 1.4. Summary of literature on CL|MPL interface study**

| Reference                           | Investigated Properties                                                | Approach                                                         | Materials                                                                                    | Key Findings                                                                                                                                                                                                                                                                                                                                                             |
|-------------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Kleemann <i>et al</i> (2009) [106]  | CL MPL interfacial resistance                                          | Numerical modeling                                               | MPL: unspecified<br>CL: unspecified                                                          | <ul style="list-style-type: none"> <li>Cell compression significantly affects potential loss at 1 Acm<sup>-2</sup> (up to 170 mV)</li> </ul>                                                                                                                                                                                                                             |
| Kim <i>et al</i> (2009) [107]       | CL MPL interfacial voids                                               | Modeling combined with HFR measurements                          | MPL: Sigracet 10BB<br>CL: Gore 5710 CCM                                                      | <ul style="list-style-type: none"> <li>Interfacial delamination causes an increase in total cell resistance</li> </ul>                                                                                                                                                                                                                                                   |
| Swamy <i>et al</i> (2009) [108,109] | Cell compression, CL MPL interfacial morphology, resistance            | Numerical modeling, optical profilometry                         | MPL: Sigracet 10BB<br>CL: unspecified                                                        | <ul style="list-style-type: none"> <li>Contact resistance increases due to the presence of CL MPL interfacial voids</li> <li>CL MPL interfacial contact is affected by local compression pressure, elasticity of the MPL, surface morphology of materials</li> <li>40% drop in contact resistance is achieved with a 50% drop in MPL and CL surface roughness</li> </ul> |
| Bajpai <i>et al</i> (2010) [105]    | CL MPL interfacial properties                                          | Numerical modeling, experimentally determined surface morphology | MPL: (80µm thick)<br>CL: Gore (10 µm)                                                        | <ul style="list-style-type: none"> <li>At 1 Acm<sup>-2</sup>, the potential decreases by ~54 mV by the addition of interfacial layer.</li> <li>Local void at MPL CL increases ohmic losses by ~37mV, and when it is filled with water, the overpotential increases by ~25 mV</li> </ul>                                                                                  |
| Hizir <i>et al</i> (2010) [101]     | CL MPL interfacial morphology                                          | Optical profilometry                                             | MPL: Sigracet 10BB<br>CL: unspecified                                                        | <ul style="list-style-type: none"> <li>MPL surface has a higher roughness and dominates local transport and interfacial contact resistance</li> <li>Level of roughness can be on the order of 10 mm peak height and contributes to a significant water storage capacity (~6-18%)</li> </ul>                                                                              |
| Zenyuk <i>et al</i> (2013) [104]    | Cell compression, CL MPL interfacial morphology and contact resistance | Modeling, experimentally determined surface morphology           | Case study 1: MPL: Sigracet 10BC, CL: ion power<br>Case study 2: MPL: MRC U105, CL: Gore CCM | <ul style="list-style-type: none"> <li>Interfacial contact resistance is independent of cracks</li> <li>Water storage capacity of the cracked CL MPL is higher by an order of magnitude compared to the smooth interface</li> </ul>                                                                                                                                      |
| Kalindini <i>et al</i> (2013) [103] | Cell compression, CL MPL                                               | Modeling, experimentally determined surface morphology           | MPL: Sigracet 10BB<br>CL: unspecified                                                        | <ul style="list-style-type: none"> <li>CL MPL significantly affects the performance at high current density region (1 Acm<sup>-2</sup>)</li> <li>The interfacial voids account for 20% reduction in the limiting current density</li> </ul>                                                                                                                              |
| Tabé <i>et al</i> (2015) [102]      | CL MPL interfacial morphology                                          | Instantaneous Freezing method                                    | MPL: Sigracet 25BC and BA<br>CL: Gore Primea 5570 CCM                                        | <ul style="list-style-type: none"> <li>CL MPL interfacial gaps provide space for liquid water accumulation</li> <li>The absence of gaps as shown in a GDE-based MEA improve performance at higher current densities</li> </ul>                                                                                                                                           |

| Reference                        | Investigated Properties                         | Approach                                                   | Materials                                                                                                                 | Key Findings                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|----------------------------------|-------------------------------------------------|------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Prass <i>et al</i> (2016) [110]  | Cell compression, CL MPL interfacial morphology | X-ray micro computed tomography                            | MPL: Sigracet 25BC<br>CL: Vulcan XC-72R (pseudo CL)                                                                       | <ul style="list-style-type: none"> <li>Small gaps are found throughout the CL-MPL interface by the surface roughness features of the layers</li> <li>A higher compression lowers the fraction of interfacial gaps</li> </ul>                                                                                                                                                                                                                                    |
| Aoyama <i>et al</i> (2016) [111] | CL MPL interfacial morphology                   | Cryo SEM for cross-section imaging, fuel cell polarization | MPL: Freudenberg-NOK<br>CL: unspecified                                                                                   | <ul style="list-style-type: none"> <li>No water accumulation at the CL MPL made by GDE method, where CL is deposited directly on MPL</li> <li>The MEA made with GDE method shows lower mass transport loss</li> </ul>                                                                                                                                                                                                                                           |
| Nozaki <i>et al</i> (2017) [112] | Flow field type, CL MPL contact firmness        | Freezing and cryo SEM, fuel cell polarization              | Hydrophilic MPL: Carbon fiber (40 $\mu\text{m}$ ),<br>Hydrophobic MPL: VulcanXC72R (15 $\mu\text{m}$ )<br>CL: unspecified | <ul style="list-style-type: none"> <li>Narrow land/channel flow field reduces interfacial gaps and thus improves cell performance</li> <li>With hydrophobic MPL, the interfacial gap can be as wide as 2 <math>\mu\text{m}</math>, which causes potential drop <math>\sim 0.3</math> V at <math>1.5</math> A/cm<sup>2</sup></li> <li>Hydrophilic MPL (40 <math>\mu\text{m}</math>) imposes narrower interfacial gaps compared to the hydrophobic MPL</li> </ul> |

## 1.6 Research Objectives and Thesis Layout

Based on the literature review in Sections 1.5 and 1.6, a further improvement in several areas is required to raise the competitiveness of PEM fuel cells particularly in the emerging automotive applications. The goal of this study is to improve the operational flexibility of the PEM fuel cell by optimizing water management in different areas of the PEM fuel cell at lower Pt loading in the CCL ( $\sim 0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ), which is becoming the future benchmark for the fuel cell CL. In this work, water management issues, which include dehydration of the membrane under drying conditions and flooding of the catalyst layer under wet and high current operation, were addressed by the modification of the interfaces of the catalyst layer, namely the PEM|CL interface and the CL|MPL interface.



**Figure 1.11: Thesis Layout**

In this thesis, **Chapter 1** provides introduction and literature review on energy, particularly for the use in transportation sector, fundamentals, history and milestones of fuel cell. It also covers the scope of study and approaches used to bridge the research question formulated from the literature review. **Chapter 2** describes all the synthesis methods used in this research as well as all the physical and electrochemical characterization methods used in this work. This includes metal loading quantification, crystallite size measurement, proton conductivity measurement, cross-sectional imaging, ECSA calculation, and polarization measurement. All the protocols and conditions for MEA testing are also explained in detail. Figure 1.11 summarizes the thesis layout and structure.

As discussed in section 1.6.2, the application of chemical deposition (or electroless deposition) of a Pt layer in the membrane subsurface can potentially improve membrane performance under dry conditions. The other advantages of this method include its reproducibility and suitability for a larger scale manufacturing. Thickness, loading and interconnectivity of Pt particles are variables that determine the functionality of this structure. It is therefore necessary to understand the effects of those variables on the performance of the fuel cell under different conditions. **Chapter 3** shows the effects of synthesis parameters, especially reduction time on the resulting structure of the electroless Pt layer at the PEM|CL interface and also to the performance of the fuel cell. **Chapter 4**, on the other hand, examines the new architecture of an MEA with a microporous layer directly deposited on the CCL of a CCM. This new architecture shows a reduction in the interfacial gaps between the catalyst layer and microporous layer (CL|MPL interface) which leads to reduced water pooling near the catalyst layer, and thus improving fuel cell performance. A number of variables are varied and examined

to determine the optimum composition on the MPL such as thickness and carbon type. **Chapter 5** provides the conclusions of this thesis work and recommendations for future work that can be built on from the findings of this research.

## Chapter 2: Experimental Procedure

### 2.1 Synthesis

In this thesis, two new structures, namely electroless Pt in the membrane subsurface and modified MPL on the catalyst layer were synthesized and applied to a GDE-based and CCM-based MEA, respectively.

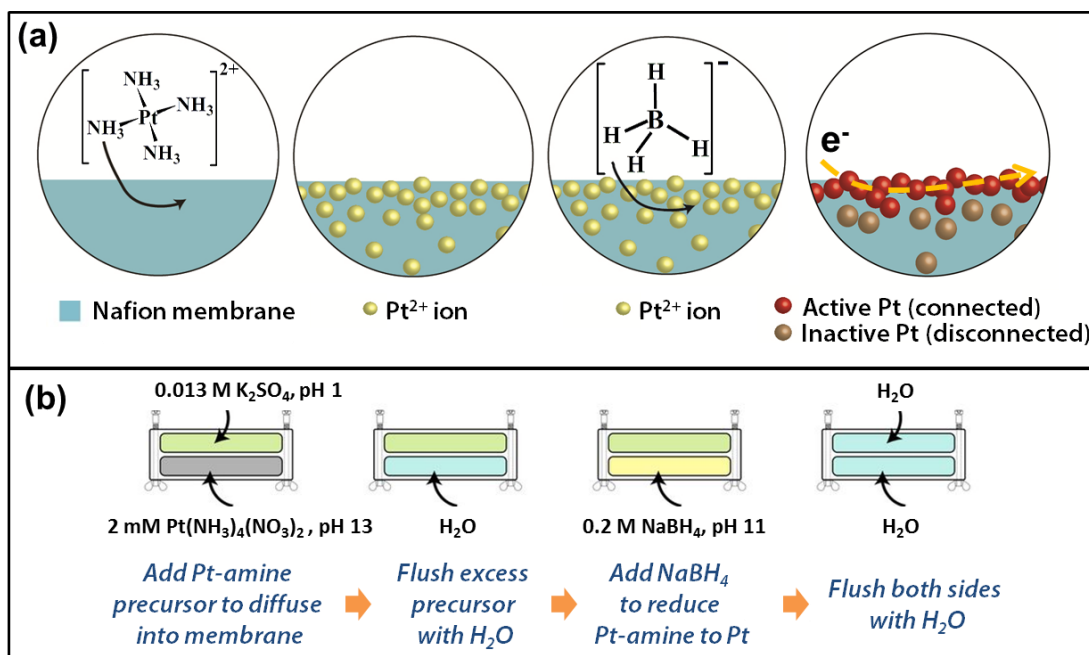
#### 2.1.1 Electroless Pt Layer

Electroless Pt layer synthesis method was adopted from previously published work with a modification of reaction temperature, i.e., 30°C instead of 35°C [62]. Figure 2.1 shows the four main steps (i.e., pre-cleaning, impregnation, reduction and post-cleaning) used for the electroless Pt deposition process. The description of the synthesis steps are as follows:

1. **Pre-cleaning:** The reinforced Nafion membrane was soaked with deionized (DI) water at 22°C (18.2 MΩ cm, <5 ppb TOC water, Milli-Q Integral 5, Fisher Scientific Company) for more than two hours in order to hydrate the membrane. Furthermore, this step ensured higher hydration of the membrane and increases the availability of the deposition sites in the membrane.
2. **Impregnation:** After the pre-cleaning step, the membrane, with an exposed area of 7 cm × 11 cm, was mounted in the deposition cell (see Figure A.4) where it was exposed to a 0.013 M solution of K<sub>2</sub>SO<sub>4</sub> (adjusted to pH 1 with 0.1 M H<sub>2</sub>SO<sub>4</sub>) on one side and a 2 mM solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (adjusted to pH 12 using KOH) on the other side, for a period of 30 minutes. The temperature of the cell was controlled at 30°C by placing the cell in a water bath (Isotemp 6200R28, Fischer Scientific Company). To seal the perimeter of the membrane, the membrane was cut with a slightly larger size (~12.5 cm × 9 cm). This extra

area was sandwiched tightly in the cell in order to provide better sealing of the membrane. After the impregnation step,  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  solution was removed from its compartment, and the compartment on that side was rinsed with DI water twice while keeping the  $\text{K}_2\text{SO}_4$  solution in its compartment.

3. **Reduction:** A 0.2 M solution of  $\text{NaBH}_4$ , adjusted to pH 11 with an appropriate amount of  $\text{KOH}$ , was added immediately to the empty compartment and was allowed to react for 2 to 16.5 min while the solutions on both sides were stirred manually with a pipette. After this reduction step, the solutions of both compartments were immediately removed, and the membrane was flushed twice with DI water.
4. **Post-cleaning:** The resulting electrolessly Pt-deposited membrane was then soaked in a 5 M solution of  $\text{HClO}_4$  for more than 48 hours in order to remove any residual Pt ions, and then followed by several DI water rinsing steps.



**Figure 2.1:** (a) In-situ electroless Pt deposition process consisting of impregnation of the Pt-amine ions into the membrane and reduction of Pt-amine ions by borohydride ions, and (b) schematics of synthesis steps in a deposition cell with chemicals used on both sides.

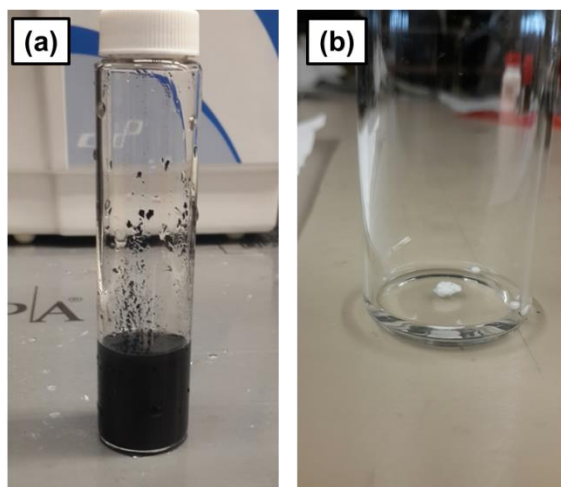


### 2.1.2 Modified Microporous Layer (MPL)

The modified MPL synthesis method used in this study consists of Carbon Black solution preparation, Teflon solution preparation, MPL ink preparation, ink spraying, and post treatment. These steps are described as follows:

1. Carbon black solution: Carbon black solution (Figure 2.2a) was prepared by mixing carbon black and isopropanol with a composition of  $\sim 0.5$  mL per mg carbon black. After mixing, the solution was sonicated in a water bath sonicator for  $>30$  min.
2. Teflon solution preparation: Teflon solution (Figure 2.2b) was prepared by mixing 1% by weight of PTFE AF 1600 (Sigma-Aldrich) granules in Perfluoro-compound FC-72 (ACROS Organics,  $>90\%$ ). The FC-72 solvent will dissolve the PTFE AF 1600 granules after  $\sim 4$ h elapsed time.
3. MPL ink preparation: The Teflon solution (20% wt with respect to the carbon + Teflon loading) was mixed with the carbon black solution, and further diluted again with isopropanol to prepare the MPL ink.
4. Ink spraying: The MPL ink was sprayed uniformly on the cathode side of CCM (i.e., cathode catalyst layer) until the desired MPL loading was achieved. During spraying, the CCM was heated to  $\sim 90^\circ\text{C}$  using a hot-plate placed underneath the CCM to accelerate isopropanol evaporation. To control the deposition area, the CCM used was cut larger than the desired surface area, then a mask made of rubber with a size similar to the active area is applied. The CCM used (Johnson-Matthey) consisted of  $0.1\text{ mg}_{\text{Pt}}\text{cm}^{-2}$  at the cathode,  $0.04\text{ mg}_{\text{Pt}}\text{cm}^{-2}$  at the anode, and a reinforced perfluorosulfonic acid-based membrane ( $17\text{ }\mu\text{m}$ ).
5. Post treatment: The modified CCMs (i.e., CCMs with a sprayed modified MPL) were heat-treated in a muffle furnace (Barnstead Thermolyne, type 48000). The final weight of the

MPL was determined by subtracting the initial weight from the final weight of the MPL after the solvent evaporated.



**Figure 2.2: Photographs of MPL ink components: (a) the mixture of carbon black and isopropanol, and (b) granules of PTFE AF1600 dissolved in a perfluorinated solution**

## **2.2 Physical Characterization**

### **2.2.1 Cross Sectional Image**

Scanning Electron Microscopy (SEM) is a tool used for magnification of conductive specimens ( $50\text{--}10^5\times$ ). SEM produces magnified images by rastering the specimen surface with an electron beam. The signal used to construct images results from secondary and back-scattered electrons. The secondary electrons are the electrons ejected with low energy from the atom after interaction with the electron beam, and hence are more sensitive for surface characterization. On the other hand, back-scattered electrons are the electrons produced from elastic collisions between beam electrons and atoms, which change the trajectory of the electrons. They emerge from a deeper region of the specimen and dependent on the interaction with the colliding atoms. This characteristic therefore renders them useful for providing information of the composition of the scanned sample. In a backscattered electron image, heavier elements with larger atoms

scatter more electrons to create more signal or a brighter image than the lighter elements. Similar to SEM, Transmission Electron Microscopy (TEM) also operates using electron beams to produce a signal from the observed image. In TEM, unlike SEM, the high energy beam of electrons is transmitted through a very thin specimen instead of being reflected and thus produces a higher spatial resolution. Such a high resolution is useful for providing information about the crystal structure and morphology of the specimen.

In this work, SEM was used to obtain cross-sectional images of the electrolessly-deposited membranes and MPLs. Samples for cross-sectional SEM imaging were prepared by cryo-fracturing the samples placed in a specimen stub in liquid nitrogen. To ensure the conductivity of the membrane cross-section, all electrolessly-deposited membrane samples were coated with a 10 nm thick carbon layer using a precision modular high-vacuum sputter coating instrument (Leica EM MED 020, Leica Microsystems Inc.). All images were obtained using a dual beam FEI Helios Nanolab 650 scanning electron microscope operating with an accelerating voltage of 2 kV and an emission current of 0.2 nA.

The Pt particles distribution throughout the membrane for electrolessly-deposited membrane samples was also examined by transmission electron microscopy (TEM, FEI Tecnai G2 200 kV, ThermoFischer Scientific). To prepare thin films (50-100 nm) for TEM FEI Tecnai G2 200 kV imaging, the samples were encased in epoxy and sectioned with ultramicrotomy (Leica UC7 ultramicrotome with a Diatome diamond knife to cut the samples). The occupancy of Pt particles was determined using the grey scale method analyzed with ImageJ software. Pt occupancy on a horizontal 1D line at a given distance from the membrane surface was determined by comparing the pixels occupied by Pt particles and by non-deposited membrane in a cross sectional TEM image. The black pixels represented the Pt particles, and white pixels

represented the membrane non-occupied by Pt particles. The thickness of the deposited electroless Pt was estimated by the point at which the Pt particles occupy more than 50% of the space.

### 2.2.2 Crystallite Size

X-ray diffraction is generated by the elastic scattering of X-ray photons by atoms in a periodic lattice. The scattered X-rays in an ordered lattice that interfere constructively result in a peak as a function of scattering angles ( $2\theta$ ). The width of the peak then can provide further information on the crystallite size. In this work, the crystallinity of the deposited Pt in the membrane subsurface was determined by an X-ray powder diffractometer (XRD, D2 Phaser Diffractometer, Bruker Corporation) using a Cu  $K\alpha$  radiation source and a Lynxeye<sup>TM</sup> detector. The X-ray scans were collected for a scattering angle ( $2\theta$ ) range of  $20^\circ$  to  $80^\circ$  at a rate of  $0.02^\circ \text{ s}^{-1}$ . Five consecutive iterations were performed in order to obtain an improved signal to noise ratio. The crystallite size was estimated using the following Scherrer equation [113]:

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (2.1)$$

where  $D$  is the crystal size (nm),  $\lambda$  is the  $K\alpha$  radiation wavelength of copper (0.154 nm), and  $B$  is the full width at half maximum of the Bragg peak at  $2\theta$  (radian).

### 2.2.3 Platinum Loading

In this research, the Pt loading for electroless Pt layers synthesized was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF).

### 2.2.3.1 Inductively Coupled Plasma Optical Emission Spectrometry

Inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical tool for qualitative and quantitative determination of trace elements in a sample with high precision. For a solid sample such as metal catalysts, the sample is usually digested with acid and diluted with a matrix solution (e.g., low concentration nitric acid). The sample solution is then converted into an aerosol followed by a quick evaporation upon the delivery to the center of the plasma, which is maintained at 7000 – 10000 K. When energy is added due to collisional excitation within the plasma, the atoms get promoted into excited states. The excited state species may then relax to the ground state and emit photons. The wavelength of the photons emitted can be used to identify the elements in the sample. The total number of photons is directly proportional to the concentration to the element identified.

The Pt loading of electrolessly-deposited membrane was determined by inductively coupled plasma optical emission spectroscopy (Agilent 725 ICP-OES, equipped with an auto-sampler and radial view, Agilent Technologies Canada Inc.). Samples for ICP-OES analysis were prepared by digesting the electrolessly-deposited Pt membrane samples in aqua regia solution, which was prepared by mixing 0.67 mL of concentrated hydrochloric acid and two mL of concentrated nitric acid. To prepare a sample for ICP-OES analysis, three pieces of electrolessly-deposited membrane ( $\varnothing = 6$  mm each) were cut from different locations of the membrane and digested in the aqua regia solution for 45 minutes and heated gradually from 75 to 250°C. The clean and digested membrane pieces were then removed from the solution, and the solution was diluted to 25 mL volume with 2% nitric acid solution. The 25 mL solution was divided into two samples to perform duplicate ICP-OES measurements. A series of standard Pt

solutions with different concentrations were prepared from dilution of a Pt standard solution (Isospec Delta, catalog number 78-01-12/100, 1000 ppm, Delta Scientific Laboratory Products Ltd.). The measured loadings were determined by averaging concentrations from four different emitted Pt wavelengths using the K emission lines. Statistical errors were determined by the standard deviation of the averaged loading values from four chosen Pt wavelengths.

#### **2.2.3.2 X-Ray Fluorescence**

Quantitative assessment of Pt loading (in  $\mu\text{g cm}^{-2}$ ) in the electrolessly-deposited membranes was also performed by X-ray fluorescence spectroscopy (XRF, Fischerscope X-Ray XDV-SDD, Fischer Technology Inc.) using a micro focus tube with a beryllium window X-ray source, 1000  $\mu\text{m}$  Al filter, 1000  $\mu\text{A}$  anode current, 1 mm collimator diameter and a 50 kV beam voltage. Baseline substrate correction was performed with a pristine membrane (Johnson Matthey). The XRF scans were performed on a 14 - 66  $\text{cm}^2$  grid of 100 equally-spaced points and a counting time of 10 s per spot.

#### **2.2.4 Conductivity or Resistivity**

In-plane sheet resistance was obtained using a four-point probe (Model S-302-4, Signatone Corporation) resistance measurement connected to a Potentiostat (BioLogic Science Instruments). A tungsten carbide probe head was used with a 0.004" tip spacing, 0.010" tip radius, and 45 g pressure (SP4-40045TBY). The resistance of each point was determined by calculating the gradient of the voltage-current curve obtained from applying cyclic voltammetry from -0.5 V to 0.5 V at room temperature (21°C) and humidity (~40%). The results were averaged over five cycles. The resistance, R, of the platinized membrane was obtained from an

average of nine different points across the sample ( $3 \times 3$  grid with a 1 cm margin from the edges), and the volume resistivity was calculated using the following equation:

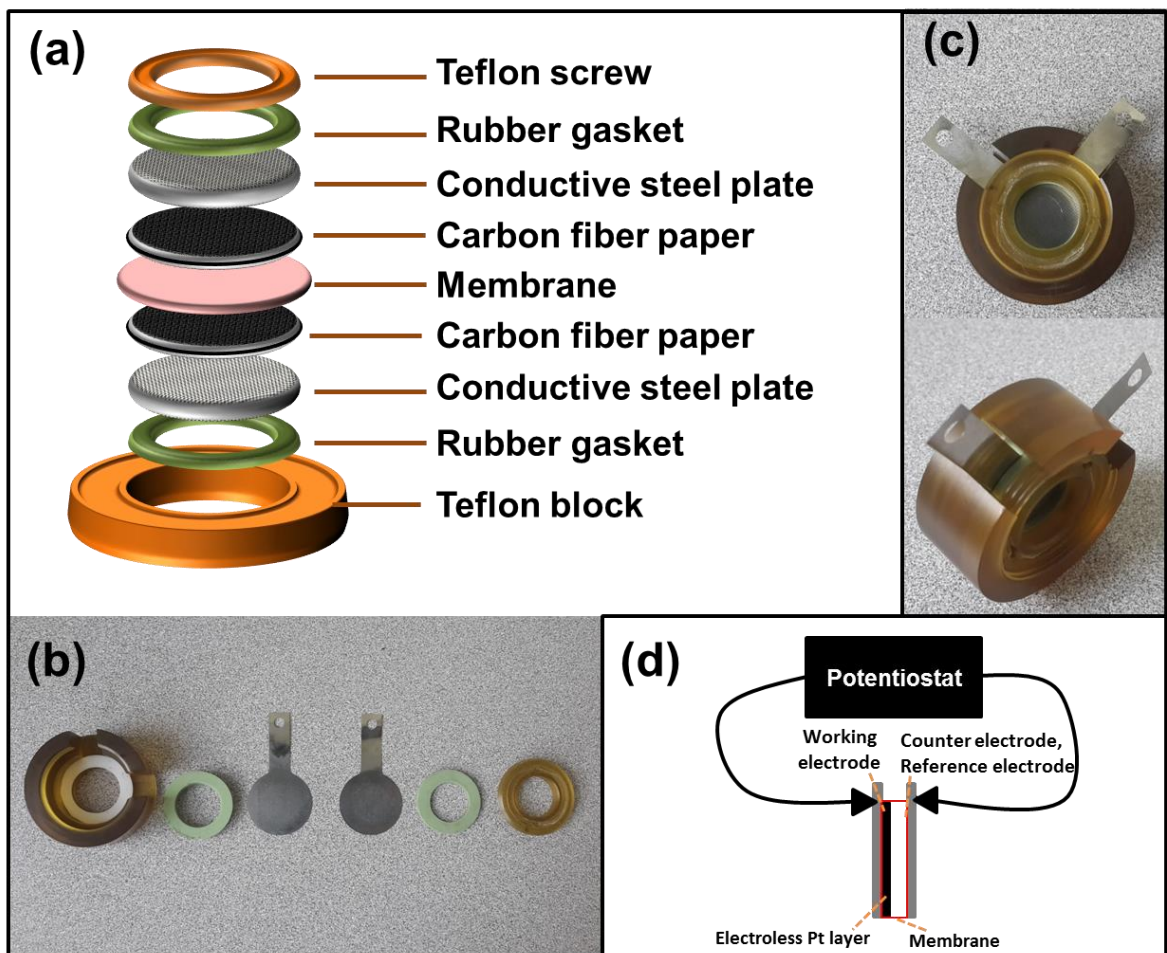
$$\sigma = \frac{\ln(2)}{\pi} \times \frac{1}{k \times R \times t} \quad (2.2)$$

where  $\sigma$  is the in-plane conductivity ( $\text{S cm}^{-1}$ ),  $k$  is the probe correction factor,  $R$  is the resistance of the sheet obtained from the gradient of the  $V - I$  curves, and  $t$  is the thickness of the sample (cm). The correction factor ( $k$ ) of the probe accounts for separate factors including the ratio of the probe spacing to sample size and the ratio of sample thickness to probe spacing [114]. Statistical errors were determined from the standard deviations obtained from averaging nine different resistivity values across the sample.

Through-plane conductivity of the Pt-deposited membranes was determined using a two-probe electrochemical cell set-up with a similar design to that of Soboleva *et al* [115]. Figure 2.3 shows the schematic and the components of the cell used in this work. The two-probe cell used consisted of two hollow gaskets, two perforated metal-coated plates, a hollow Teflon block, and a Teflon screw. Membranes for testing were cut to a diameter of 2.54 cm and sandwiched by the perforated metal-coated plates. Two pieces of carbon fiber papers with the same diameter were placed on each side of the membrane to ensure connectivity between the plates and the membrane. Prior to the conductivity measurements, a blank cell (with no membrane) was tested to extract the impedance of the plates and carbon paper alone. To ensure the consistency of the pressure exerted by the cell, the Teflon screw was tightened to the similar position for all measurement. The average resistance of the cell hardware was determined by averaging three measurements and this value was subtracted from all resistance measurements to obtain the real membrane resistance. To measure conductivity at different conditions, the cell was placed in a

closed beaker ( $\varnothing = 5.5$  cm, height = 7 cm) with a ventilation hole and contacted with air under controlled humidity and temperature (flow rate = 0.8 NLPM). Impedance measurements were performed by performing potentiostatic electrochemical impedance spectroscopy (PEIS) from 0.2 kHz to 80 kHz using a SP-150 Biologic potentiostat. Each reported measurement is an average of three different measurements. The baseline measurements were performed with three different samples. The pressure applied was lower than 28 psi as indicated by the absence of color change of an ultra-low pressure paper (range of 28 – 85 psi, Fujifilm LLW, Fujifilm Corporation) test. The cell hardware resistance (i.e., with no membrane sample) was measured and subtracted from the reported values to eliminate the contribution of cell hardware and carbon fiber papers.





**Figure 2.3: (a) Schematic of the cell used to measure through plane proton conductivity, (b) photo of the components of the dissembled cell, (c) and (d) photos of the assembled cell**

Through-plane resistance of MEAs tested with a single cell was also measured for every current density of polarization cycles. Resistance measurements were performed at a frequency of 2.5 kHz with an AC voltage amplitude of 0.2 V using a GWistek LCR 821 instrument attached to the cell.

### 2.2.5 Static Contact Angle and Immersion Test

The static contact angle values reported here were averaged from three different measurements using three different spots on the sample with the error bars representing the

standard deviations of these measurements. The contact angle measurements were performed by dropping a droplet of water (10  $\mu$ L) on the surface of MPL aggregates deposited on a piece of Kapton (Matrix Technology). To prepare the MPL aggregates, following steps were performed: i) the MPL ink was sprayed in a ceramic plate, ii) the sprayed ceramic was heat treated according to the MPL fabrication protocol, iii) MPL aggregates were peeled from the ceramic plate, and iv) aggregates were compressed into a condensed layer with a flat surface. The contact angle photos were taken using FTA121110 – Falcon apparatus (equipped with blue LED backlight) and software FTA32. For the immersion test at room temperature, the MPL aggregates obtained after heat treatment were immersed in  $\sim$ 30 mL DI water placed in a beaker at the room temperature ( $\sim$ 21°C). The beaker then was heated to 80°C on a hot plate to simulate the behavior of the aggregates at the fuel cell operating temperature (80 °C).

#### **2.2.6 Water Diffusion across Membrane**

The apparatus set-up used in this work was adapted from a previously published work [116] and is shown in Figure S5. The Tandem TP5 (active area of 5 cm<sup>2</sup>) fuel cell hardware from Tandem Technologies with serpentine flow fields, on either side of the membrane, was used to conduct the experiments. The cell was fed by water on the anode side and gas with various humidity levels on the cathode side. The catalyzed membrane samples were sandwiched by a pair of carbon Toray fiber papers (T090, 20% PTFE, FuelCellStore) and placed between the anode and cathode flow fields. The temperature of the cell was maintained at 80°C using hot water circulated from a water bath, while the compression pressure was regulated at 100 psi by a pneumatic piston sandwiching the cell. The temperature of the chilling water for the condenser ( $\sim$ 90% efficiency) was maintained at 2°C, and the water condensed in the line was absorbed by a

calcium sulfate adsorbent (Drierite, AlfaAesar). The amount of water transferred through the membrane was determined by differential weighing of the adsorbent before and after each experiment. All the values measured were subtracted by the initial water content (before passing the cell) to isolate the water that had diffused through the membrane. The baseline sample (i.e., the bare membrane) refers to a zero electroless Pt loading ( $0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ).

## 2.3 Electrochemical Characterization

There were three electrochemical characterizations used in this study: cyclic voltammetry (CV) for electrochemical surface area (ECSA) quantification, linear sweep voltammetry (LSV) and open circuit voltage (OCV) for hydrogen crossover, and current-voltage polarization for fuel cell overall performance.

### 2.3.1 Electrochemically Active Surface Area

Cyclic voltammetry (CV) is a technique to measure catalyst activity by measuring current response of an electrode over a potential range under an inert gas environment. CV measurements employed in this study used the potential range where hydrogen absorption and desorption occur ( $0.05 - 1.2 \text{ V vs. RHE}$ ). Current response to the potential sweep is shown as a peak in the cyclic voltammogram (a plot of current vs. potential in CV measurement). The active catalyst surface area commonly known as electrochemically active surface area (ECSA, in  $\text{m}^2 \text{ g}_{\text{Pt}}^{-1}$ ) of the samples were calculated from the area of the hydrogen desorption ( $H_{\text{upd}}$ ) region using the following equation:

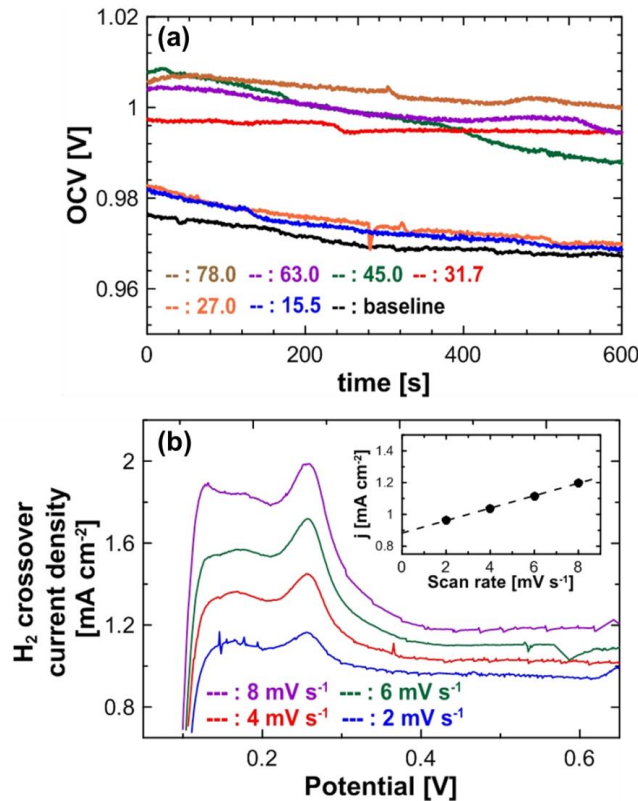
$$\text{ECSA} = \frac{q_{\text{Pt}}}{\Gamma \times M_{\text{Pt-grain}}} \quad (2.3)$$

where  $q_{Pt}$  represents the charge density ( $\mu\text{C cm}^{-2}_{\text{geometric}}$ ) of the hydrogen desorption peak,  $\Gamma$  represents the charge required to reduce a monolayer of hydrogen on platinum ( $210 \mu\text{C cm}^{-2}_{Pt}$ ), and  $M_{Pt\text{-grain}}$  represents the Pt loading ( $\text{g}_{Pt} \text{ cm}^{-2}_{\text{geometric}}$ ). The charge density,  $q_{Pt}$ , was calculated by integration of hydrogen desorption area to avoid any contribution from hydrogen evolution in the hydrogen adsorption area [117].

### 2.3.2 Gas Crossover

Hydrogen crossover for the electroless Pt work was determined by two methods: i) open circuit voltage (OCV) hold, and ii) linear sweep voltammetry (LSV). The OCV hold was performed in the Tandem TP-5 cell for 15 minutes by sandwiching a membrane with a pair of the commercial GDEs ( $0.3 \text{ mg}_{Pt} \text{ cm}^{-2}$ ), one on each side. The cell was fed with pure hydrogen (99.999%, 5.0 ultra-high purity, Praxair) on the anode side (0.1 NLPM, 60 kPag) and oxygen (Praxair, 99.993% purity) on the cathode side (0.2 NLPM, 60 kPag). With the LSV method, samples were exposed to pure hydrogen on the anode side (0.07 NLPM, 60 kPag) and nitrogen (Praxair, 99.998% purity) on the cathode side (0.1 NLPM, 60 kPag). The hydrogen flowrates used in this study (i.e.,  $14$  and  $20 \text{ mL min}^{-1} \text{ cm}^{-2}_{\text{electrode}}$ ) are typical in the hydrogen crossover experiment, i.e.,  $8 - 22 \text{ min}^{-1} \text{ cm}^{-2}_{\text{electrode}}$  [31,118–120]. The potential of the samples was then scanned from  $0.05$  to  $0.85 \text{ V}_{\text{RHE}}$  using four different scan rates ( $8, 6, 4,$  and  $2 \text{ mV s}^{-1}$ ), and the potential at  $0 \text{ mV s}^{-1}$  derived from the extrapolation of these results, was used to calculate hydrogen crossover [121]. Gases in all experiments were maintained at a temperature of  $80^{\circ}\text{C}$  and a relative humidity of  $100\% \text{ RH}$ . For the LSV method, the response current at  $\sim 0.4 \text{ V}$  vs. the anode is taken as the hydrogen crossover current. This hydrogen crossover current is generally

known as the limiting hydrogen oxidation current because beyond this potential, the hydrogen will instantly be oxidized due to the high overpotential [121–123]. In the traditional LSV method, the limiting hydrogen potential is used to calculate the hydrogen crossover flux with the Faraday's law. Pei *et al.* point out that the value of the limiting hydrogen oxidation current depends on the LSV sweep rate, which was also observed in this work (Figure 2.4) [121]. Furthermore, Pei *et al.* also propose to use the limiting hydrogen oxidation current at  $0 \text{ mV s}^{-1}$  by extrapolating the plot of limiting current at  $0.4 \text{ V}$  vs. sweep rate to determine the hydrogen limited potential.



**Figure 2.4: (a) OCV hold for 10 minutes of hydrated MEAs (1 h hydration) with different electroless Pt loadings, (b) an example of LSV scan of a baseline sample with different scan rates ranging from 2 – 8  $\text{mV s}^{-1}$  and extrapolation to obtain crossover current density at  $0 \text{ mV s}^{-1}$  (inset figure).**

### 2.3.3 Polarization Curve

A  $j$ - $V$  or polarization curve was used in this study to characterize the overall performance of an electrode or an MEA. A polarization curve shows the potential response of an electrode or an MEA to the current applied. During the measurement, each current is held for a few minutes (2-5 min) until a steady state voltage is reached, which then can be used as the valid cell potential response. Test conditions (such as cell temperature, cell humidity, cell compression pressure, anode gas flow rate, anode gas temperature, anode gas pressure, anode gas humidity, cathode gas stoichiometry, cathode gas temperature, cathode gas pressure, and cathode gas humidity) affect the fuel cell performance significantly and therefore need to be controlled during a measurement. A test station (Greenlight G100 and G20) with high precision control over the aforementioned variables is generally used to run the polarization measurements.

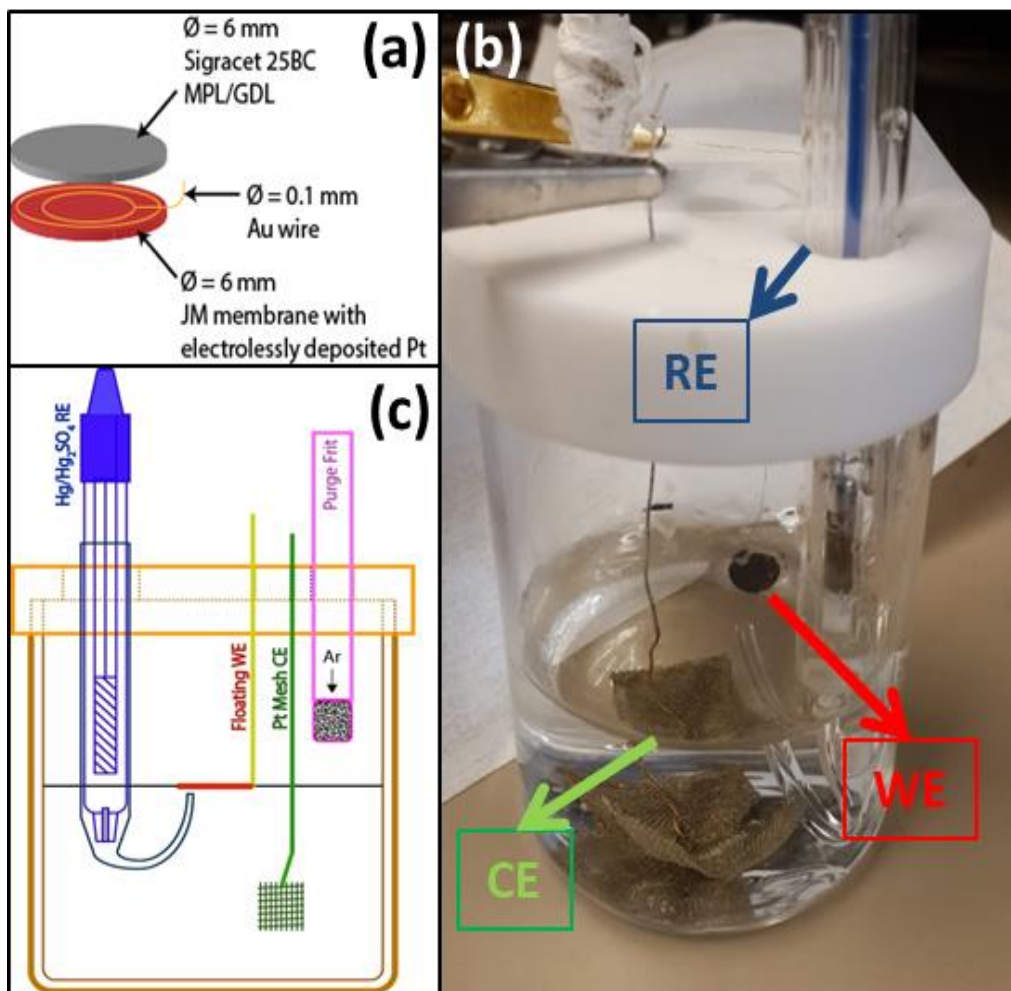
IR-corrected or IR-free polarization curves are a type of polarization curve that can be generated by subtracting the potential loss contributed by the through-plane ohmic resistance at the raw potential measured. Since the ohmic loss is excluded, the IR-free polarization curve is typically characterized by a nearly plateau profile in the ohmic region. This IR-free polarization curve is useful to determine the kinetic and mass transport losses from an electrode or MEA.

In this study, anode and cathode gas, and cell temperatures were set fixed at 80°C, while the flow rate, gas humidity, and cell compression were varied according to the cell used and the objective of each test. G20 or G100 Greenlight test station (Greenlight Innovation) was used in this research to control temperature, pressure, flow rate, and cell compression during the measurements.

## 2.4 Testing Apparatus and Conditions

### 2.4.1 Floating Cell

A floating cell or electrode [124] for electrochemical surface area (ECSA) quantification was prepared by hot pressing a platinized membrane with an area of  $0.28 \text{ cm}^2$  ( $\varnothing = 6 \text{ mm}$ ) with coiled gold wires ( $\varnothing = 0.1 \text{ mm}$ , 99.95%, Alfa Aesar) and a Sigracet 29BC GDL/MPL layer with a similar size as the platinized membrane is shown in Figure 2.5(a). All the samples were hot-pressed (Dake Model 44226) at 250 psi and  $160^\circ\text{C}$  for 5 min. The electrochemically active surface area (ECSA) was obtained using the cyclic voltammetry (CV) technique with a potential range of 0.05 to 1.2 V vs. RHE using four different scan rates (500, 100, 50, and  $20 \text{ mV s}^{-1}$ ) under an inert argon gas environment. A potentiostat (5A board, Bio-Logic VMP3) was used for potential control and data acquisition. For all testing, an Hg/Hg<sub>2</sub>SO<sub>4</sub> (0.5 M H<sub>2</sub>SO<sub>4</sub> filling solution) reference electrode (Radiometer Analytical) in a Luggin capillary and a Pt flag counter electrode were used. The reference electrode was regularly calibrated to the reversible hydrogen electrode (RHE) in each electrolyte concentration and the potential scale shifted accordingly. To clean the samples, a number of electrochemical cleaning cycles were initially performed by scanning the samples reversibly from 0.05 to 1.2 V vs. RHE under argon at a rate of  $500 \text{ mV s}^{-1}$  until steady state CVs were achieved. On average about 600 cleaning cycles were performed for each sample.



**Figure 2.5: (a) Floating electrode set-up used to determine the electrochemical active surface area, (b) photo of the assembled floating electrode cell, and (c) schematics of the components of a floating electrode**

## 2.4.2 Half-cell

The half-cell is a fuel cell testing platform that allows electrode performance evaluation in a more realistic environment with better time and cost effectiveness. The widely used rotating disk electrode (RDE) testing approach uses a very thin ( $\sim 0.3 - 0.4 \mu\text{m}$ ) and small area of catalysts, which has a different layer composition and geometry than a real fuel cell catalyst layer. As a result, RDE-measured catalyst activities may not necessarily be adequate to predict the performance in a  $\text{H}_2/\text{O}_2$  fuel cell architecture. On the other hand, the single cell or fuel cell



testing approach requires large quantities of materials such as catalyst, and is time consuming and complex. In this regard, the half-cell bridges the gap to enable a testing platform which still resembles the simplicity and testing speed of the RHE but allows for characterization of catalyst performance at higher current densities (up to  $1500 \text{ mA cm}^{-2}$ ) and more closely represents the performance of a single cell.

A detailed description of the half-cell design used is provided in Appendix 5.2A.1. Perchloric acid ( $\text{HClO}_4$ ) was selected as the electrolyte rather than sulfuric or phosphoric acid due to the well-known issue of bi(sulfate) and phosphate anion adsorption on Pt-based catalysts [125].  $\text{HClO}_4$  solutions were prepared from concentrated acid (70%, Veritas Double Distilled, GFS Chemicals) and DI water. All half-cell testing was carried out at ambient temperature ( $\sim 20^\circ\text{C}$ ) to minimize the safety risks associated with  $\text{HClO}_4$  and prevent electrolyte decomposition [126]. The potentiostat for potential control, reference electrode, and counter electrode are similar to that of the floating cell set up. The relative positioning of the electrodes is key to reducing the cell resistance; the Pt flag is placed in front of the working electrode sample holder while the tip of the Luggin capillary is placed to the side to prevent shielding errors, as shown in Figure 2.6. The Luggin capillary should be no closer than two times the tip diameter from the working electrode surface [127].

For half-cell testing, circular samples ( $\text{Ø} = 20 \text{ mm}$ ) were punched from a larger sheet. The exposed active area ( $\text{Ø} = 15.6 \text{ mm}$ ,  $1.91 \text{ cm}^2$ ) was delimited by the size of the o-ring. To produce samples which also had a membrane layer with electroless Pt, a platinized membrane was hot pressed directly on the GDE. The platinized membrane and GDE were sandwiched between two PTFE plates and hot pressed (Dake Model 44226) at  $160^\circ\text{C}$  and 250 psi for 5 min. Higher

pressure was not used in order to prevent damage to the porous structure of the MPL and GDL. Samples with membrane were pre-hydrated before testing by storing in DI water for > 24 hrs.



**Figure 2.6: Photo of assembled half-cell in electrochemical cell**

### **2.4.3 Single Cell or Fuel Cell**

Fuel cell performance tests were conducted with three different cells: Standard Test Cell (Ballard Power), TP50 (Tandem Technologies), and TP5 (Tandem Technologies). For each test, the cell used was connected to a 2 kW Hydrogenics Fuel Cell (G100, Greenlight Innovation) or a 100 W Hydrogenics Fuel Cell (G20, Greenlight innovation). The test station feeds water with a controlled temperature to the testing cell to maintain the cell temperature. The test station also controls the reactant gas pressure, gas flow rate, gas temperature, and gas dew point temperature, with the last two parameters used to determine or change the gas humidity. The procedure for any test involves: (i) leak testing, (ii) MEA conditioning, and (iii) performance testing.

#### **1. Leak Testing**

Leaks in the hydrogen gas line are detected using a hydrogen detector TIF 8850 while hydrogen gas is flowing in the line. Rapid beeping produced by the detector indicates hydrogen

leaks from the line (accuracy 5 ppm). Leaks, which mainly come from line fittings or connections, can also be indicated by a gradual decrease of hydrogen pressure in the line when the line is closed at both ends.

## 2. MEA Conditioning

MEA activation or conditioning is performed before testing for a number of purposes: (i) hydration of the Nafion membrane and ionomer network in the catalyst layer, (ii) removal of contaminants, and (iii) performance stabilization to obtain a similar starting condition for all MEAs tested. Previous studies have shown that the effective conditioning of the MEA can be achieved by holding the MEA at a potential of around 0.5 - 0.7 V for a longer duration (i.e., 12 - 19 h) [128–130]. In this research, the MEAs tested were conditioned for 6 – 12 h depending on the type of cell used at 100% RH and a constant current of 500 mA cm<sup>-2</sup>.

## 3. Performance testing

Test conditions (gas pressure, cell compression, gas humidity, size of the active area, and cell type) used in this study were varied according to the purpose of the test except for the gas temperature that was set at 80°C. A summary of the test conditions with the corresponding cell used are listed in Table 2.1.

### 2.4.3.1 Fuel Cell Tests for Electroless Pt Layer Study

For the electroless Pt layer (Chapter 3), the MEA size of 45 cm<sup>2</sup> (5 cm × 9 cm) and 1D parallel channel fuel cell (Ballard Power STC) at high cathode stoichiometry were used to reduce the effect of gas concentration effects and transport limitations. These 1D fuel cells are important for the study of kinetic performance and parameters in this work. The polarization performance of the baseline presented was an average of three different MEAs tested. Throughout the testing,

air was fed to the cathode with a stoichiometry of 10, whereas pure hydrogen was fed to the anode with a stoichiometry of 1.5 (100 kPag, 80°C). Before polarization tests, all MEAs were conditioned at 100% RH, 500 mA cm<sup>-2</sup> for 12 h. Three consecutive polarization cycles at 100% RH were performed on each MEA with 15 min intervals (held at 500 mA cm<sup>-2</sup>) between each cycle to regain the MEA potential stability. Resistance measurements were performed at a frequency of 1 kHz with an AC voltage amplitude of 0.2 V using a GWinstek LCR 821 instrument for each current density.

To initiate low humidity conditions prior to polarization measurements at 30% RH, each MEA was conditioned at 500 mA cm<sup>-2</sup> for 1 h at 30% RH using a stoichiometry of 10. A high flow rate was used to purge the high humidity air remaining in the humidifier and lines and to equilibrate the MEA and the system at 30% RH. A shorter interval (i.e., 5 min) was used between 30% RH polarizations because there was no MEA flooding and to prevent decay of the MEA performance due to drying. This protocol was maintained consistently for all tests conducted. For humidity cycling, a constant current of 500 mA cm<sup>-2</sup> was applied to the assembled MEA for 6 hours at 100% RH, followed by 6 hours at 30% RH, and finally 6 hours at 100% RH.

For the long-term humidity cycling test, a constant current of 500 mA cm<sup>-2</sup> was applied to the assembled MEA for 6 hours at 100% RH, followed by 6 hours at 30% RH, and finally 6 hours at 100% RH.

#### **2.4.3.2 Fuel Cell Tests for Modified MPL Study**

For the Modified MPL study (Chapter 4), the MEA size used was 5 cm<sup>2</sup> (2.3 cm × 2.3 cm) and 14 cm<sup>2</sup> (2 cm × 7 cm) in TP5 and TP50 cell, respectively. The MEAs used for testing in

TP50 are masked in order to reduce the amount of limited materials available for this research (e.g., the CCM and Teflon AF 1600). The impact of masking an MEA in TP50 on the performance is discussed in Appendix 5.2A.3. Both TP5 and TP50 cells use counter-flow single serpentine bipolar plates. As listed in Table 2.1, the low stoichiometry of 2 was used on the cathode and 1.5 on the anode for the high humidity tests (RH= 100%). For the low humidity tests, a higher cathode stoichiometry of 8 was used to accelerate drying.

**Table 2.1. Conditions of fuel cell testing and the corresponding cell used.**

| <b>Analyzed Area</b>                      | <b>Cell Used</b>   | <b>Type of test</b>                             | <b>Condition</b>                                          | <b>MEA size (width × length)</b> | <b>Test protocol</b>                                                         |
|-------------------------------------------|--------------------|-------------------------------------------------|-----------------------------------------------------------|----------------------------------|------------------------------------------------------------------------------|
| Electroless Pt layer for PEM CL interface | Standard test cell | Wet polarization (100% RH)                      | Cell compression: 60 psi<br>gas pressure: 100 kPag        | 5 cm × 9 cm                      | Polarization measurement is repeated 4x with a 15 minute interval in between |
|                                           | Standard test cell | Dry (30% RH)                                    |                                                           | 5 cm × 9 cm                      | Polarization measurement is repeated 3x with a 5 minute interval in between  |
| Modified MPL for CL MPL interface         | TP50               | Wet polarization (100% RH)                      | Cell compression: 100 psi<br>gas pressure: 150 kPag       | 7 cm × 2 cm                      | Polarization measurement is repeated 2x with a 15 minute interval in between |
|                                           | TP5                | Wet polarization (100%), dry polarization (20%) | Cell compression: 80 psi<br>gas pressure: 100 or 150 kPag | 2.3 cm × 2.3 cm                  | The current density is hold at 500 mA/cm <sup>2</sup> for 2 hours            |

## Chapter 3: PEM | Catalyst Layer Interface<sup>2</sup>

### 3.1 Introduction

As discussed in Section 1.5.2, the presence of deposited Pt particles in the membrane subsurface (Figure 3.1) offers more performance benefits especially for membrane electrode assemblies (MEAs) fabricated by the combination of a pair of gas diffusion electrodes (GDEs) and a membrane, which has an interfacial gap between the membrane and catalyst layer. Electroless deposition of Pt in the membrane has been used and developed significantly from the original method of *Takanaka-Torikai* to *Impregnation-Reduction*, *non-equilibrium Impregnation-Reduction*, and the recent *modified non-equilibrium Impregnation-Reduction* to synthesize such a structure. Table 3.1 shows the summary of the main reported electroless deposition methods available in literature.

The recent deposition variable tuning for the modified non-equilibrium I-R method has allowed for a deposition of a low loading ( $<0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ) and dense-thin ( $<200 \text{ nm}$ ) Pt layer with improved Pt utilization [61,62]. This well developed, simple, and scalable synthesis method was further modified and used in this study to synthesize a number of platinized membranes with low Pt loadings. In this chapter, the first systematic study of the effect of the deposition parameter on the physical structures and the behavior of platinized membranes with relatively low Pt loadings ( $<0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ) in a thin PFSA-based membrane ( $17 \text{ }\mu\text{m}$ ) synthesized with the *modified non-equilibrium I-R* method is presented. The effect of reduction time on the loading

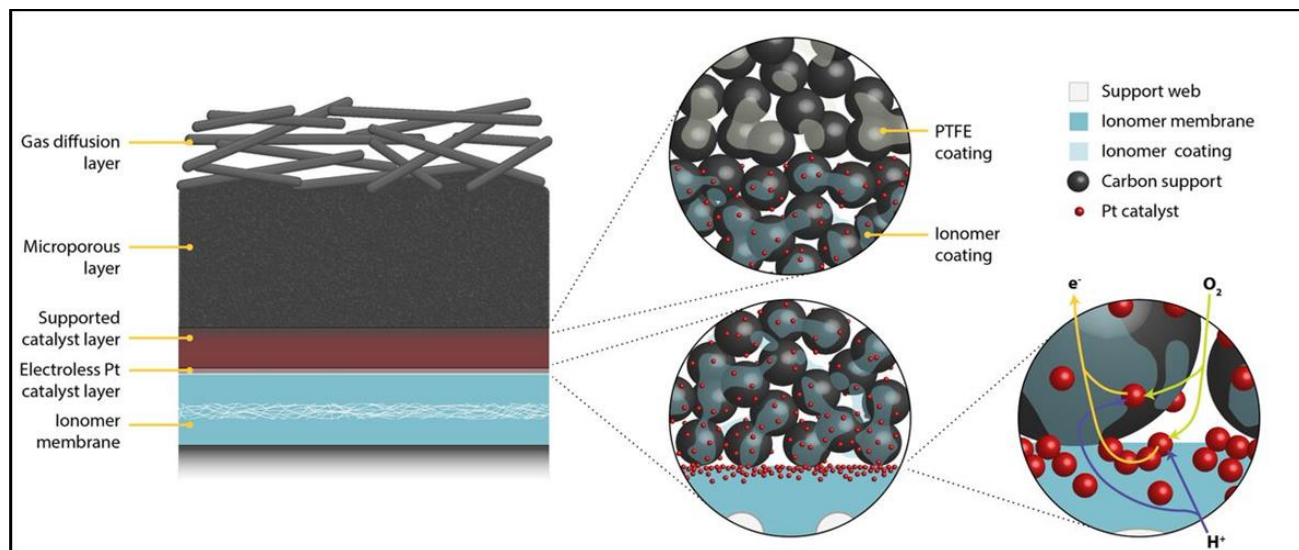
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<sup>2</sup> Sections of this work have been published in:

Daniel, L.; Bonakdarpour, A.; Wilkinson, D. P. “Relationship between Electroless Pt Nanoparticle Growth and Interconnectivity at the Membrane Interface: Implications for Fuel Cell Applications.” *ACS Appl. Nano Mater.* **2019**, 2, 3127–3137

Daniel, L.; Bonakdarpour, A.; Wilkinson, D. P. “Benefits of Platinum Deposited in the Polymer Membrane Subsurface on the Operational Flexibility of Hydrogen Fuel Cells.” *Journal of Power Sources*, **2020**, 471, 228418

and structure of electrolessly-deposited Pt nanoparticles in the membrane, particularly at the lower Pt loading range is discussed in Section 3.2. The platinized membranes were carefully characterized by a number of analytical techniques to obtain accurate correlations between the Pt nanoparticle loading and their interconnectivity within the Nafion membrane. The variation of the electrochemically active surface area with the impregnated Pt content and simple relationships between the ECSA, Pt utilization and the grain dimensions were investigated and are presented in Sections 3.3 - 3.7. The effects of electrolessly deposited Pt in the membrane subsurface on hydrogen crossover, oxygen reduction reaction catalytic performance, proton conductivity, and overall PEMFC performance at high and low humidity are analyzed in Sections 3.8 - 3.10.



**Figure 3.1: Schematics of (a) MEA with an electroless Pt layer in membrane subsurface**

**Table 3.1. Summary of the reported Pt electroless or chemical deposition methods and loadings obtained**

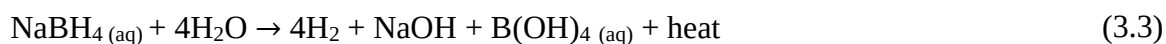
| <b>Method</b>                | <b>Description</b>                                                                                                                                                       | <b>Loading<br/>(mg<sub>Pt</sub> cm<sup>-2</sup>)</b>           |
|------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| Takanaka-Torikai (T-T)       | One-step deposition by which a metal precursor is in contact with one side of the membrane and a reductant is in contact with the other side                             | 1-6 [37], 2-5 [131], 3.2 [132], 1.0 [133]                      |
| Impregnation-Reduction (I-R) | Two-step deposition by which the membrane first is ion-exchanged with a metal precursor followed by the reduction of the impregnated membrane by a reductant             | 2-6 [38], 1.13 [55], 1.0[134] , 0.5-3.5 [135] , 0.02-0.06 [34] |
| Non-equilibrium I-R          | Two-step deposition (similar to I-R) with the impregnation step of a metal precursor into the membrane is not carried to the equilibrium state                           | 0.55 [39], 1.2 [136], 0.25 [60], 2.0 [137]                     |
| Modified Non-equilibrium I-R | Two-step deposition (similar to non-equilibrium I-R) with a high pH of Pt precursor and a low pH of K <sub>2</sub> SO <sub>4</sub> solution during the impregnation step | ~1-2 [62], 0.05-0.08 [63], 0.083-0.382 [64],                   |

### 3.2 Deposition Time, Pt layer Loading, and Layer Uniformity

Figure 3.2a shows that the Pt loading, as determined by ICP-OES, increases almost linearly with the reduction time up to a maximum loading of  $\sim 70 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ . At this near-saturated loading ( $\sim 12 - 16.5$  min reduction time), the reduction of Pt ions appears to diminish, and the Pt content becomes independent to the reduction time. The reduction of Pt tetraamine solution ( $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ) with sodium borohydride ( $\text{NaBH}_4$ ) occurs according to the following redox reaction [138]:



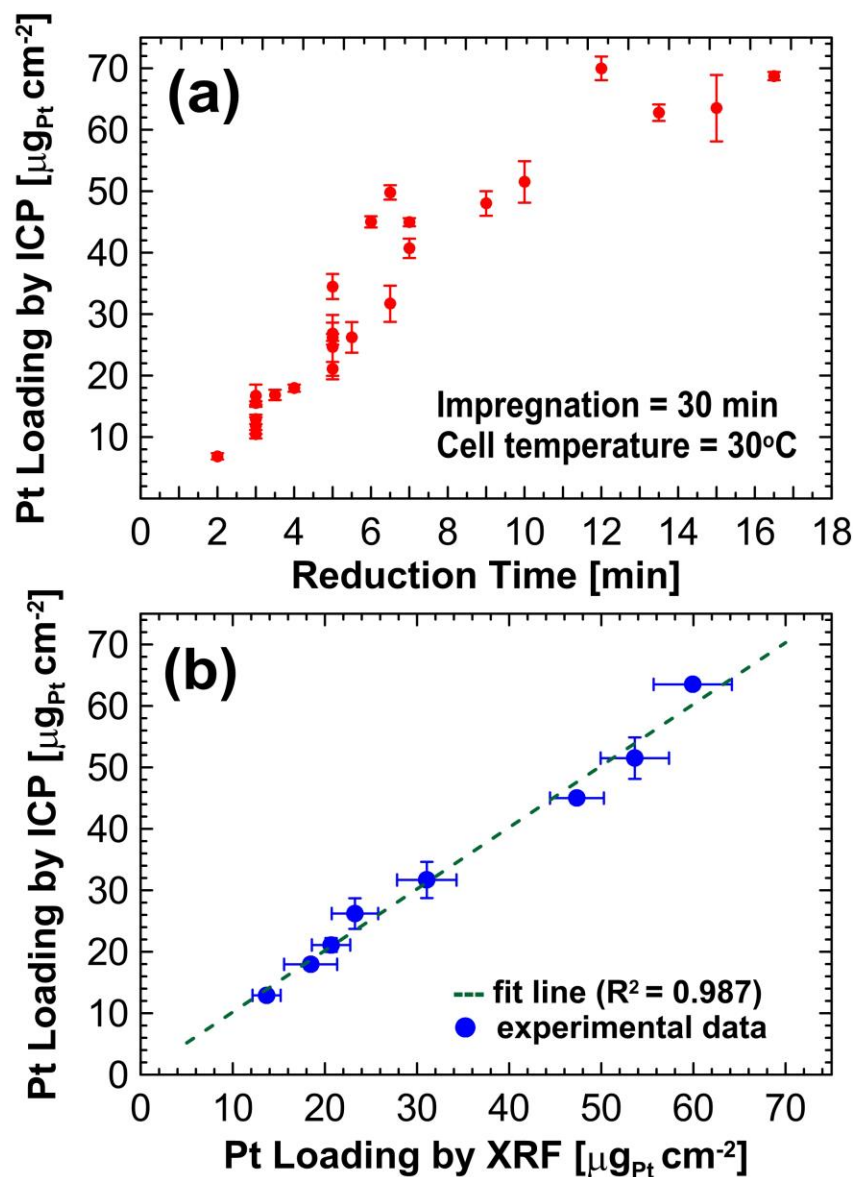
The hydroxyl ions needed for this reaction are produced from the hydrolysis of the borohydride ions represented in the following reaction [138,139]:





This reaction is also known as the decomposition of borohydride in water, which usually occurs rapidly as a result of the poor stability of borohydride ions in water. The rate of the decomposition of borohydride is dependent on the pH of the solution. At higher pH, for instance with the addition of NaOH, the rate is reduced and therefore the stability of the borohydride is improved [61,139]. In this synthesis process, a low pH of 1 was used (regulated by the  $\text{K}_2\text{SO}_4$  solution) to create a thin Pt layer in the subsurface. This low pH environment resulted in a higher decomposition rate of borohydride as indicated by the rapid hydrogen gas production during the reduction step.

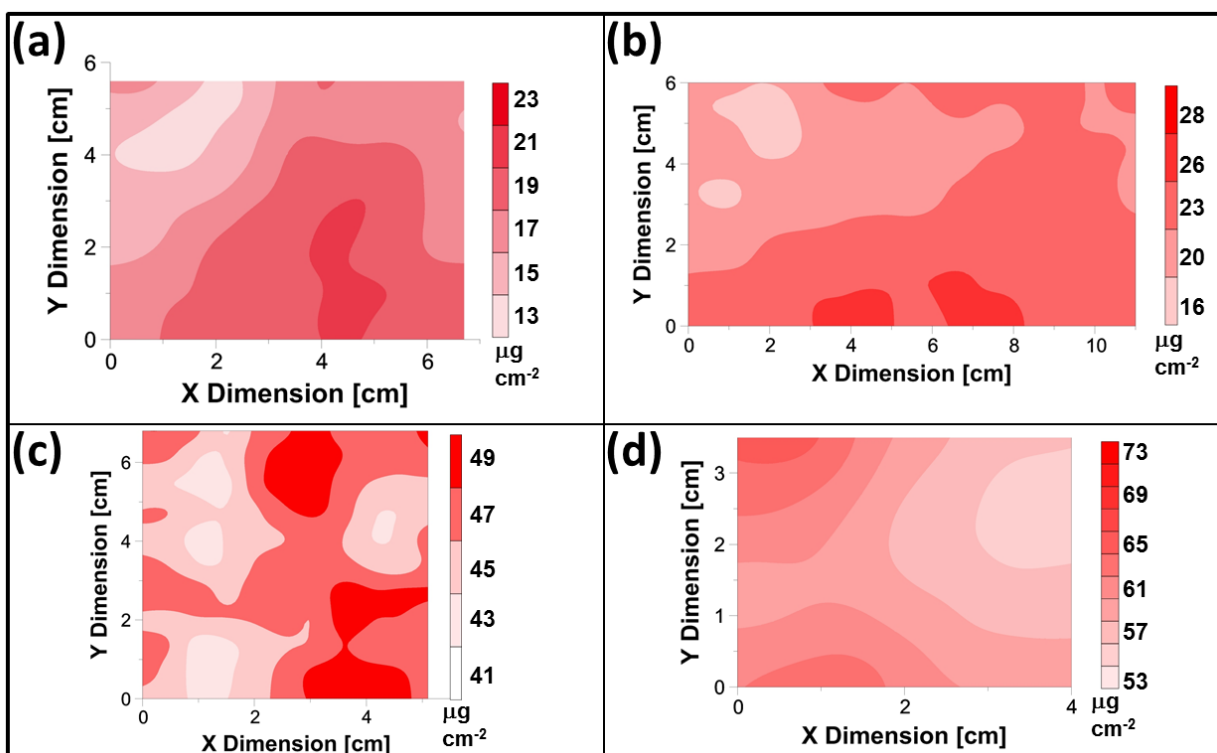
Based on a stoichiometric molar balance calculation (i.e., nine moles of  $\text{BH}_4^-$  for reduction of four moles of  $\text{Pt}^{2+}$ ) [58], at the highest loading achieved in this work, only ~56% of the  $\text{BH}_4^-$  ions were used for Pt reduction. Rapid decomposition of borohydride to hydrogen in water is most likely the main cause of the loss of the borohydride ions (Equation 3.3). A denser and thicker Pt layer built in the membrane subsurface can also cause limitation of the diffusion of the borohydride ions into the membrane, which further limit the growth of the Pt sublayer loading as a function of the reduction time.



**Figure 3.2:** (a) Pt loading as a function of reduction time, and (b) comparison between Pt loading determined by ICP-OES and a 100-point average of XRF measurements across the surface.

The homogeneity of the Pt loading distribution across the membrane was examined by XRF mapping of a sample using a  $10 \times 10$  grid analysis map and the averaged loadings were compared with the ICP-OES results (Figure 3.2b). The correlation between both the two sets of data is excellent ( $R^2 = 0.99$ ) indicating that the Pt content, quantified by ICP-OES at any

loadings shows good agreement with averaged loadings from the XRF measurements. Distribution of Pt particles at different loadings is quite uniform across the membrane surface area but shows ~10 - 15% lower loadings near the edges (Figure 3.3). The lower loadings may result from the hydrogen bubbles which are formed during the reduction step and appear to be more severe at the top of the cell where there was insufficient stirring action. Mapping of the Pt loading suggests that the loading value at the center of the platinized membrane was very close to the average value of the Pt loading and was therefore used for any subsequent analysis.



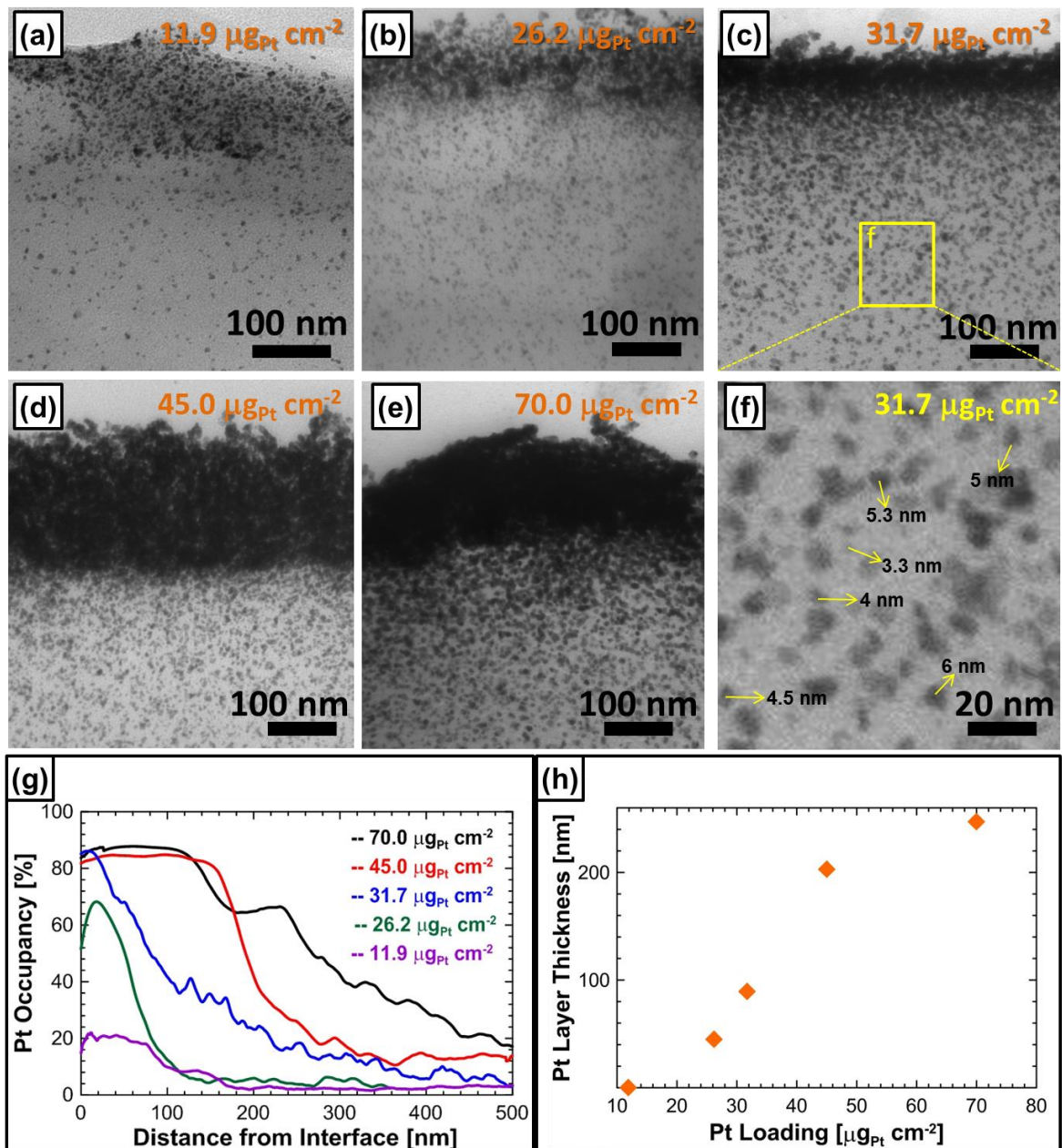
**Figure 3.3: Loading distribution of Pt in membrane with a loading of (a) 18.0, (b) 26.2, (c) 45.0, and (d) 63.5  $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  respectively measured by XRF.**

### 3.3 Cross Sectional Imaging of the Pt Layer

Figure 3.4a-e show the TEM analysis of Pt thickness and density for a series of electrolessly-deposited Pt layers with various Pt loadings. The individual Pt grain size,

approximated from the TEM images in the area deeper from the surface, lies in the range of 3.7 – 6.0 nm as depicted in Figure 3.4f. These are the seeds that will grow and coalesce to form bigger particle agglomerates. Figure 3.4g shows a semi-quantitative measure of the Pt particles occupancy, using the gray-scale shading, across the membrane's cross section as described in Section 2.2.1. Here, an increase in the density of the Pt occupancy (from ~20% to ~90%) corresponds to a Pt loading increase of 12.9 to 70.0  $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . An increase in the Pt layer density leads to an increased in-plane conductivity (Figure B.2, Appendix 5.2B.2) as more connected particles allow for better transport of the electron current. A rough estimate of the interconnectivity of the Pt nanoparticles can be obtained by taking the ratio of the area with higher concentration of Pt nanoparticles and the total area below in Figure 3.4g. For instance, the membrane with a Pt loading of 45  $\mu\text{g cm}^{-2}$  (red line) has a high Pt occupancy within 200 nm of the surface. Assuming all the particles in this concentrated region are connected, the ratio of this area to the total area below it provides an estimate of the Pt particle interconnectivity across the sample.

The thickness of the Pt layer grows rapidly in the beginning and appears to plateau at higher electroless Pt loadings ( $>45.0 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ) as indicated by Figure 3.4h. The occurrence of the plateau region here is similar to the loading vs. reduction time plot shown in Figure 3.2a. This limitation in achieving a further increase in the thickness of the Pt layer is attributed to the reduced diffusion and rapid decomposition of the reducing borohydride agent as the electroless Pt layer grows thicker and the instability (short lifetime) of borohydride in a low pH solution as discussed previously. The Pt layer thickness achieved with the deposition conditions employed in this work was below 250 nm, consistent with the previously reported literature data [61–63].



**Figure 3.4:** (a)-(e) TEM images of electrolessly deposited membrane with different loadings, (f) magnified TEM image to determine individual Pt particle size (g) Pt occupancy profile plot of membrane with various loadings of electroless Pt films, and (h) variation of the Pt layer thickness vs. Pt loading.

### 3.4 Crystallite Size

Figure 3.5a shows the X-ray patterns of the electrolessly-deposited membranes. All XRD patterns show the dominant Bragg (111) peak of the FCC-structured Pt at  $2\theta \approx 40^\circ$ . As Pt loading increases, the Pt (111) peak intensifies but remains centered about  $2\theta \approx 40^\circ$ . As depicted in Figure 3.5b, the (111) peak widths decrease indicating grain size growth. Figure 3.5c shows a clear linear trend between the size of Pt crystallites and the Pt content for the range of Pt loadings studied. The size of the crystallites increases almost linearly from  $\sim 1.6$  to 6 nm for the platinized membrane with loadings  $\leq 70.0 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . This quantitative observation is used in modelling the interconnectivity of deposited Pt nanoparticles in the membrane. The range of crystallite sizes reported here is comparable to the previously reported values of 2 - 6 nm obtained by transmission electron microscopy [140], the averaged size of 5.2 nm for Pt loadings in the range of 0.15 to  $0.90 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  [60,141], 5.4 - 6.7 nm for a Pt loading of  $2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  [142], and 4.7, 13.1, and 12.9 nm for 1, 2, and 3 wt% Pt in Nafion, respectively [143].

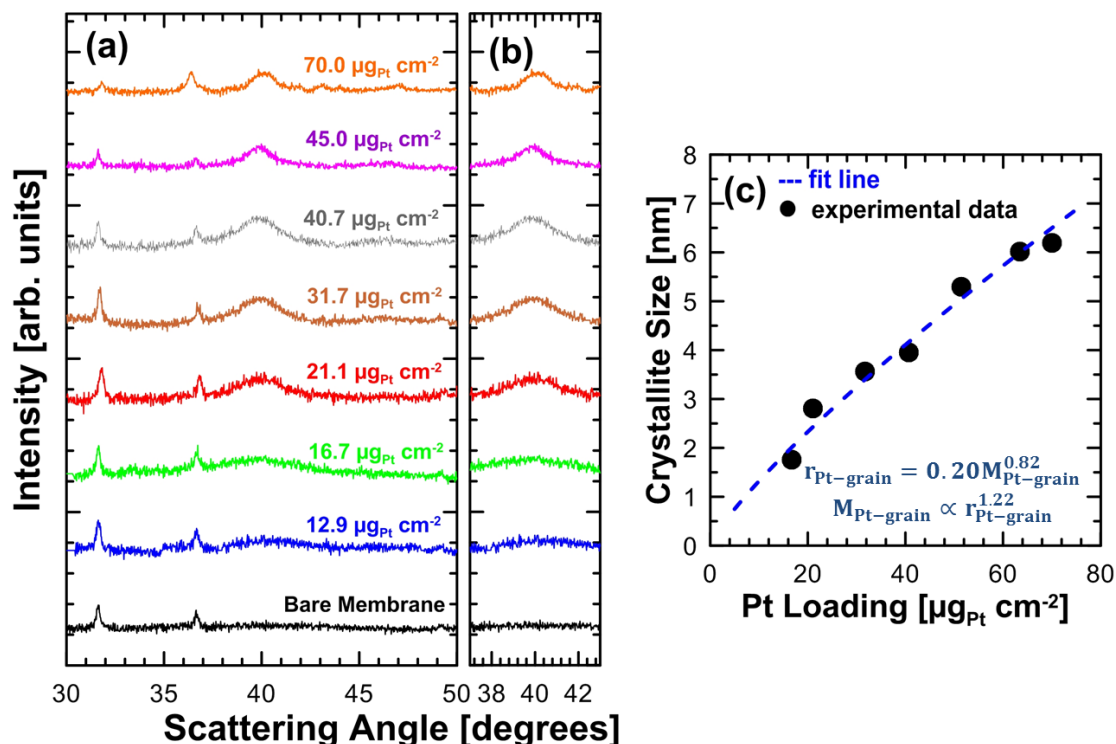
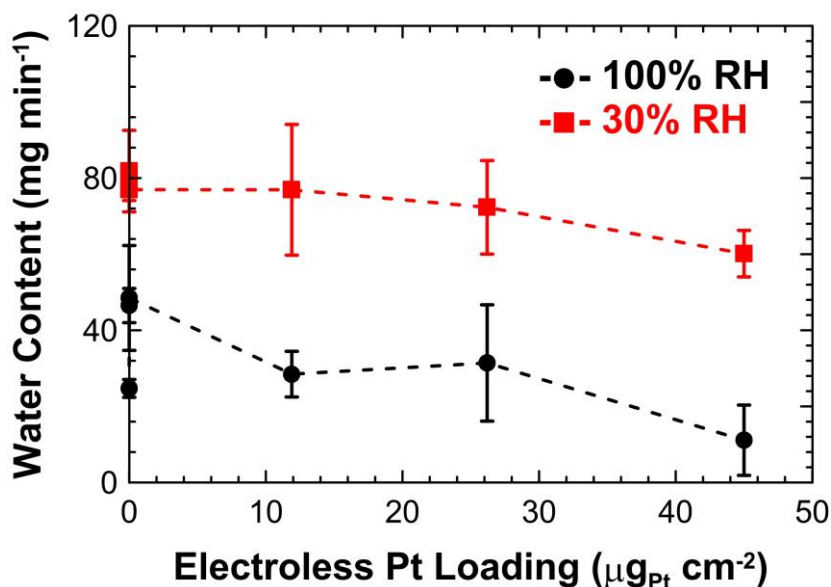


Figure 3.5: (a) X-ray diffraction patterns ( $30^\circ \leq 2\theta \leq 50^\circ$ ) of electroless Pt with different loadings ranging from 0 (undeposited membrane) to a loading of  $70 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ , (b) Pt (111) peaks for different Pt loadings, and (c) Pt crystallite size ( $r_{\text{Pt-grain}}$ ) calculated using the Scherrer equation vs. Pt loading ( $M_{\text{Pt-grain}}$ ).

### 3.5 Water Diffusion across Membrane

In this water diffusion experiment, the amount of water diffused from the anode side to the cathode side of the membrane with various electroless Pt loadings was compared to the baseline of no electroless Pt loading. Each point shown in Figure 3.6 was an average from three experiments, and the baseline was repeated with two different samples. With dry air (30% RH,  $80^\circ\text{C}$ ) flowing on the cathode side,  $\sim 80 \text{ mg min}^{-1}$  water was diffused and captured by the dry gas. Although the water diffusion decreases gradually with an increase of electroless Pt loading, the reduction is not significant, and still within the statistical error of the data. With wet air (100% RH,  $80^\circ\text{C}$ ), less water was able to be captured in the incoming air, i.e.,  $30 - 40 \text{ mg min}^{-1}$ . The general trend is similar to that of 30% RH, showing there is insignificant reduction in water

diffusion with increased electroless Pt loading in the low loading region ( $<30 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ). As the loading grows above  $40 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ , a more significant decrease is shown presumably due to high Pt particle occupancy in the hydrophilic channels of the membrane.



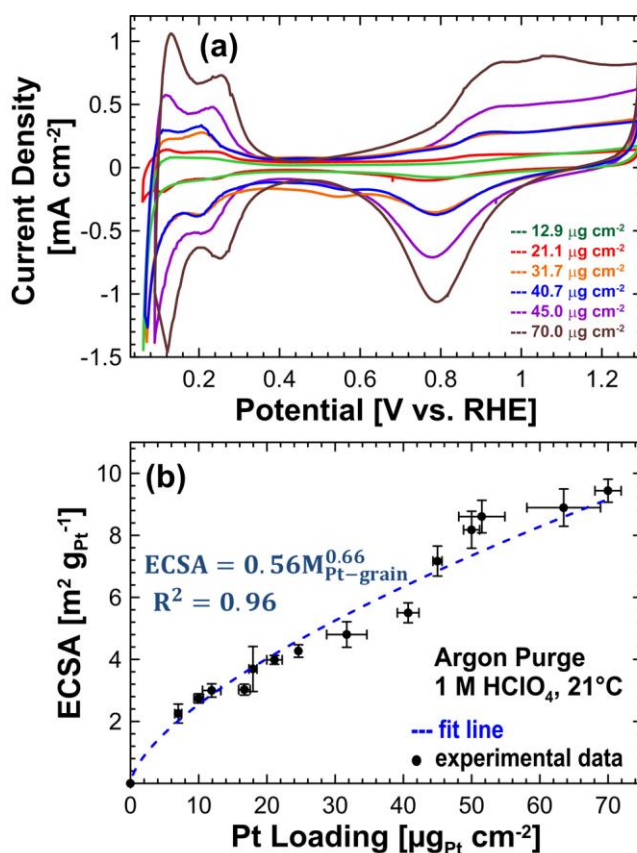
**Figure 3.6:** Water diffusion of MEAs with different electroless Pt. In this set-up, water flows on the anode side of the membrane and air at 100 and 30% humidity on the cathode side of the membrane.

### 3.6 Electrochemically Active Surface Area

The electrochemical active surface area (ECSA) is a parameter which is frequently used to determine the fraction of an electrocatalyst that is active toward an electrochemical reaction. For Pt and the oxygen reduction reaction, ECSA, which can be determined from the  $H_{\text{upd}}$  region of cyclic voltammograms, is indicative of the fraction of Pt catalyst surface available to electrons and protons, required for the electrochemical reaction. To provide an adequate supply of protons, ECSA is typically measured in a flooded electrolyte environment. Since all the ECSA measurements performed in this work were carried out in a high concentration solution (i.e., 1 M



HClO<sub>4</sub>), the only limiting factor for ECSA was the electronic conductivity of the Pt film [144,145]. Figure 3.7a shows IR-corrected cyclic voltammograms (CVs) of platinized Nafion membranes with different Pt mass areal density loadings at room temperature (21°C). The ECSA value increases with the electroless Pt loading for the loading range of 12 - 70  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  as shown in Figure 5b. It should be mentioned that the lower ECSA values observed here, compared to Pt/C catalysts layers is an indication of lower interconnectivity of the Pt nanograins within the membrane. The ECSA increases when Pt nanograin loading increases indicating that more of the Pt nanograins are in direct physical contact allowing them to conduct higher electric current during the proton adsorption/desorption of the ECSA measurements.



**Figure 3.7:** (a) IR-corrected Cyclic voltammograms of electrolessly deposited Pt in membranes with different loadings; (b) Electrochemically active surface area (ECSA) as a function of Pt loading ( $M_{\text{Pt-grain}}$ ) with a fit (dashed line) to determine the correlation between ECSA and  $M_{\text{Pt-grain}}$ . Vertical error bars indicate the standard deviation of various scan rates (500, 100, 50, 20  $\text{mV s}^{-1}$ ).

### 3.7 Pt Utilization

The increasing trend of crystallite size with Pt loading observed in Figure 3.5c can be used to determine the contribution of the grain size ( $r_{\text{Pt-grain}}$ ) and the number of grains ( $N_{\text{Pt-grain}}$ ) for a given Pt loading mass density ( $M_{\text{Pt-grain}}$  expressed in  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ). An increase in  $M_{\text{Pt-grain}}$  may result from a combination of Pt grain growth and a change in the number of grains. Assuming the Pt grains have a spherical shape (volume  $V_{\text{Pt-grain}} \propto r_{\text{Pt-grain}}^3$ ), and a fixed density ( $\rho_{\text{Pt}} = M_{\text{Pt-grain}} \times V_{\text{Pt-grain}}^{-1}$ ),  $M_{\text{Pt-grain}}$  is proportional to  $r_{\text{Pt-grain}}^3$  when the number of grains remains constant. In this case, the radius of the grains would be  $\propto M_{\text{Pt-grain}}^{0.33}$ . If the number of grains changes while the grain size increases,  $N_{\text{Pt-grain}}$  should be considered for the  $M_{\text{Pt-grain}}$  calculation. The Pt crystallites' size has the following experimental trend with respect to the loadings (Figure 3.5c):

$$M_{\text{Pt-grain}} \propto r_{\text{Pt-grain}}^{1.22} \quad \text{for } 0 \leq M_{\text{Pt-grain}} \leq 70 \mu\text{g}_{\text{Pt}} \text{cm}^{-2} \quad (3.4)$$

The ECSA measurements of Figure 3.7 can be fitted to yield the following power law for the ECSA in terms of  $M_{\text{Pt-grain}}$ :

$$\text{ECSA} \propto M_{\text{Pt-grain}}^{0.66} \quad \text{for } 0 \leq M_{\text{Pt-grain}} \leq 70 \mu\text{g}_{\text{Pt}} \text{cm}^{-2} \quad (3.5)$$

Combining Equations (3.4) and (3.5) we can express the following correlation between ECSA and  $r_{\text{Pt-grain}}$ :

$$\text{ECSA} \propto r_{\text{Pt-grain}}^{0.80} \quad \text{for } 0 \leq M_{\text{Pt-grain}} \leq 70 \mu\text{g}_{\text{Pt}} \text{cm}^{-2} \quad (3.6)$$

The above results are used to develop some understanding of the platinum grains' electrochemically active surface area (ECSA) and the utilization factor ( $\text{Pt}_{\text{utilization}}$ ). The utilization factor here refers to the ratio of the measured electrochemically active surface area (in  $\text{m}^2_{\text{Pt}}$ ) of the Pt grains to their supposedly total geometrical surface area (i.e.,  $4 \pi r_{\text{Pt-grain}}^2$ ,

expressed in  $\text{m}^2_{\text{geo}}$ ), assuming homogenous spherically-shaped grains at any given Pt loading.

Based on its definition [145], ECSA ( $\text{m}^2_{\text{Pt}} \text{g}_{\text{Pt}}^{-1}$ ) can be expressed by the following equation:

$$\begin{aligned} \text{ECSA} &= \frac{N_{\text{Pt-grains}} \times A_{\text{Pt-grain}}}{W_{\text{Pt}}} \times \text{Pt}_{\text{utilization}} \\ &= \frac{N_{\text{Pt-grains}} \times A_{\text{Pt-grain}}}{N_{\text{Pt-grains}} \times \rho_{\text{Pt}} \times V_{\text{Pt-grain}}} \times \text{Pt}_{\text{utilization}} \end{aligned} \quad (3.7)$$

where  $N_{\text{Pt-grains}}$  is the number of Pt grains,  $W_{\text{Pt}}$  is the total weight of deposited Pt (in  $\text{g}_{\text{Pt}}$ ),  $A_{\text{Pt-grain}}$  is the geometrical surface area of the grains,  $\text{Pt}_{\text{utilization}}$  (refers to the fraction of Pt grains which are connected and therefore able to conduct an electron current),  $\rho_{\text{Pt}}$  is the Pt grain density (in  $\text{g}_{\text{Pt}} \text{cm}^{-3}$ ), which is constant, and  $V_{\text{Pt-grain}}$  is the Pt grain volume ( $= 4/3 \pi r_{\text{Pt-grain}}^3$  in  $\text{cm}_{\text{Pt}}^3$ ). Equation (3.7) can be then simplified to:

$$\text{ECSA} \propto \frac{\text{Pt}_{\text{utilization}}}{r_{\text{Pt-grain}}} \quad (3.8)$$

The combination of the Equations (3.4), (3.5), and (3.6) enable us to obtain empirical relationships for the  $\text{Pt}_{\text{utilization}}$  in terms of  $r_{\text{Pt-grain}}$  or  $M_{\text{Pt-grain}}$  which are comparable to the experimental fits of  $\text{Pt}_{\text{utilization}}$  vs.  $r_{\text{Pt-grain}}$  and  $M_{\text{Pt-grain}}$  results, respectively (Figure 3.8a and b):

$$\text{Pt}_{\text{utilization}} \propto r_{\text{Pt-grain}}^{1.79} \quad \text{for } 0 \leq r_{\text{Pt-grain}} \leq 6.2 \quad \text{nm} \quad (3.9)$$

$$\text{Pt}_{\text{utilization}} \propto M_{\text{Pt-grain}}^{1.48} \quad \text{for } 0 \leq M_{\text{Pt-grain}} \leq 70 \quad \mu\text{g}_{\text{Pt}} \text{cm}^{-2} \quad (3.10)$$

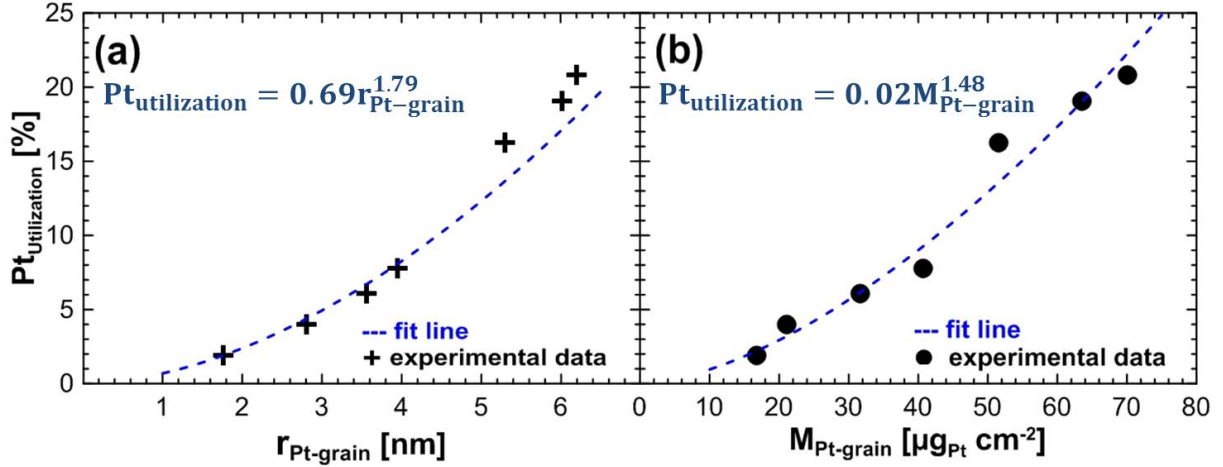


Figure 3.8: Correlation between (a) Pt utilization vs.  $r_{\text{Pt-grain}}$  and (b) Pt utilization vs.  $M_{\text{Pt-grain}}$ .

### 3.8 Gas Crossover

Hydrogen that diffuses across the membrane from the anode to cathode will react with oxygen and reduce the oxygen surface concentration. This hydrogen crossover is considered as one of the sources of membrane chemical degradation. The widely accepted mechanism to explain the chemical degradation attributes the attacks of hydrogen peroxide radicals ( $\text{HO}_2^*$ ) formed on the oxidizing cathode side in the presence of hydrogen, oxygen, and water as the cause of membrane chemical degradation. The following steps are proposed as the mechanism for the formation of hydrogen peroxide radicals on the cathode [146,147]:

- (1)  $\text{H}_2 \rightarrow 2\text{H}^*$  (via Pt catalyst)
- (2)  $\text{H}^* + \text{O}_2$  (diffusion through PEM)  $\rightarrow \text{HO}_2^*$
- (3)  $\text{HO}_2^* + \text{H}^* \rightarrow \text{H}_2\text{O}_2$
- (4)  $\text{H}_2\text{O}_2 + \text{M}^{2+} \rightarrow \text{M}^{3+} + ^*\text{OH} + \text{OH}^-$
- (5)  $^*\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^*$

The diffusion of hydrogen to the cathode also inhibits the reduction of hydrogen peroxide formed at the cathode (due to the incomplete  $\text{O}_2$  reduction) to water and hence causes the accumulation of hydrogen peroxide which can diffuse into the membrane [146]. The presence of

the additional Pt layer in the membrane subsurface reduces the gas crossover across the membrane as the diffused gases ( $O_2$  and  $H_2$ ) may react in the additional Pt layer. To the best of our knowledge, there is no gas crossover study with respect to the Pt loading of such a structure with loadings  $<0.1 \text{ mg cm}^{-2}$  as discuss in this work. Two methods were employed and compared in this work to determine the correlation between electroless Pt loading and hydrogen crossover: (i) OCV method and (ii) LSV method.

### 3.8.1 OCV Method

In the OCV method, the potential of the MEA in an  $H_2/O_2$  environment at zero current was used to calculate the hydrogen crossover. The cell potential difference at open circuit ( $\Delta V_c^{OCV}$ ), which is used to calculate the hydrogen crossover current density, denotes the difference between the thermodynamic or Nernstian OCV ( $V_c^{OCV,t}$ ) and the measured OCV ( $V_c^{OCV,m}$ ) values, and can be expressed by Equation (3.12) [17] :

$$\Delta V_c^{OCV} = V_c^{OCV,t} - V_c^{OCV,m} \quad (3.11)$$

$$\Delta V_c^{OCV} = 1.229 - 8.6 \times 10^{-4} \times (T - 298) + \frac{RT}{4F} \ln \left[ (P_{O_2})(P_{H_2})^2 \right] - V_c^{OCV,m} \quad (3.12)$$

where  $T$  is the cell temperature (K),  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $F$  is the Faraday constant ( $94865 \text{ C mol}^{-1}$ ),  $P_{H_2}$  and  $P_{O_2}$  are the partial pressures of hydrogen and oxygen (bar) respectively. In a  $H_2/O_2$  system on a Pt-based electrode, the difference between the theoretical OCV ( $V_c^{OCV,t}$ ) and measured OCV ( $V_c^{OCV,m}$ ) shown in Equations (3.11) and (3.12) is a contribution of the Pt/PtO potential mixed ( $\Delta V_{Pt/PtO}$ ) and hydrogen crossover ( $\Delta V_{crossover}$ ) [17]. The potential difference ( $\Delta V_c^{OCV}$ ), therefore, can be formulated as [148]:

$$\Delta V_c^{OCV} = \Delta V_{Pt/PtO} + \Delta V_{crossover} \quad (3.13)$$

The reaction between Pt surface and oxygen results in a mixed potential regime which is a function of temperature and the pressure of oxygen. In an acidic environment, at 80°C and 2 barg pressure,  $\Delta V_{Pt/PtO}$  is experimentally determined to be 0.12 V [17,149]. This contribution from  $\Delta V_{Pt/PtO}$  then can be subtracted from  $\Delta V_{total}$  in Equation (3.13) to obtain  $\Delta V_{crossover}$ . The relationship between  $\Delta V_{crossover}$  and the presence of an internal current at OCV can be determined from the Butler-Volmer relationship in Equation (3.14) [121] :

$$\Delta V_{crossover} = \frac{RT}{\alpha n F} \ln \left( \frac{i_{crossover}}{i_0} \times \frac{C_{r,bk}}{C_{r,s}} \right) \quad (3.14)$$

where  $\alpha$  is the transfer coefficient (taken as 0.5),  $n$  is the numbers of electrons involved,  $i_{crossover}$  is the crossover current density (in A cm<sup>-2</sup>),  $i_0$  is the exchange current density (in A cm<sup>-2</sup>),  $C_{r,bk}$  is the reactant bulk concentration, and  $C_{r,s}$  is the reactant surface concentration, respectively. When reactant is in excess, and the reaction is at equilibrium,  $C_{r,s}$  and  $C_{r,b}$  are nearly equivalent, so the last term in the bracket of the Equation (3.14) is approximately one. In this work,  $i_0$  was taken constant at  $4 \times 10^{-5}$  A cm<sup>-2</sup>, and  $i_{crossover}$  was calculated [120]. The relationship between  $i_{crossover}$  and hydrogen molar crossover rate ( $j_{H_2}$ ) can be described using Faraday's law:

$$i_{crossover} = 2 \times F \times j_{H_2} \quad (3.15)$$

where  $i_{crossover}$  is the crossover current density (A cm<sup>-2</sup>),  $F$  is the faraday constant (96,485 Cmol<sup>-1</sup>), and  $j_{H_2}$  is the hydrogen crossover molar rate (mol cm<sup>-2</sup> s<sup>-1</sup>).

### 3.8.2 LSV Method

The second method used for determination of the hydrogen crossover current was the direct LSV method with  $H_2$  and  $N_2$  as feeds to the anode and cathode, respectively [121]. Figure 3.9 shows that the hydrogen crossover current decreases with increased loading of the electroless Pt layer. The hydrogen crossover current of the bare membrane used in this work ( $\sim 0.89 \text{ mA cm}^{-2}$  (LSV) and  $0.66 \text{ mA cm}^{-2}$  (OCV) at  $80^\circ\text{C}$ ), falls within the same order of magnitude of previously reported hydrogen crossover currents for several Nafion membranes at the same temperature (Table 3.2). Table 3.2 also confirms the trend that the current density increases with a decrease of the membrane thickness.

The presence of the electroless Pt layer in the membrane subsurface reduced the hydrogen crossover current and flux with a linear trend, as indicated by both methods (Figure 3.9a and b). Although the OCV method yielded slightly lower values, the trends are apparently similar with both methods. According to the LSV measurements, the highest loading in this study (i.e.,  $78 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ) reduces the hydrogen crossover by 66% while the OCV method predicts a 37% reduction. This reduction of hydrogen crossover, which occurs in the presence of the electroless Pt layer with the low Pt loadings of  $<80 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  in the membrane subsurface regions, demonstrates the catalytic  $H_2/O_2$  recombination functionality of this layer for the hydrogen molecules diffusing to the cathode side (Figure B.5) [35]. The hydrogen crossover is, thus, reduced because of the chemical dissociation of hydrogen molecules and the reaction with the oxygen on the electroless Pt catalytic sites. Increasing the electroless Pt loading provides additional recombination sites, thus, increasing the amount of reduced hydrogen in the membrane. The mixing of the crossing hydrogen and oxygen at the catalyst layer produces hydrogen peroxide radicals that attack and deteriorate the PEM [146]. The reduction in  $H_2$

crossover flux by the electroless Pt layer in the membrane subsurface, therefore, can potentially mitigate chemical degradation and improve the lifetime of the membrane by reducing the number of hydrogen peroxide radicals in the membrane. This is particularly important for thin membranes which tend to have a higher H<sub>2</sub> crossover flux.

**Table 3.2. Summary of the reported  $i_{\text{crossover}}$  of Nafion membranes and the JM membrane used in this work at 80°C**

| Membrane             | Thickness<br>( $\mu\text{m}$ ) | $j_{\text{H}_2}$<br>( $\text{nmolcm}^{-2} \text{s}^{-1}$ ) | $i_{\text{crossover}}$<br>( $\text{mA cm}^{-2}$ ) | Method                                      | Reference   |
|----------------------|--------------------------------|------------------------------------------------------------|---------------------------------------------------|---------------------------------------------|-------------|
| JM membrane          | 17                             | 4.60                                                       | 0.89                                              | LSV                                         | this thesis |
| JM membrane          | 17                             | 3.42                                                       | 0.66                                              | OCV                                         | this thesis |
| Nafion (unspecified) | 30                             | 4.14                                                       | 0.80                                              | LSV                                         | [31]        |
| Nafion 112           | 50                             | 3.78                                                       | 0.73                                              | LSV                                         | [120]       |
| Nafion 112           | 50                             | 1.66                                                       | 0.32                                              | OCV +<br>semi-<br>empirical<br>polarization | [150]       |
| Nafion 115           | 130                            | 1.40                                                       | 0.27                                              |                                             | [150]       |
| Nafion 117           | 180                            | 1.24                                                       | 0.24                                              |                                             | [150]       |



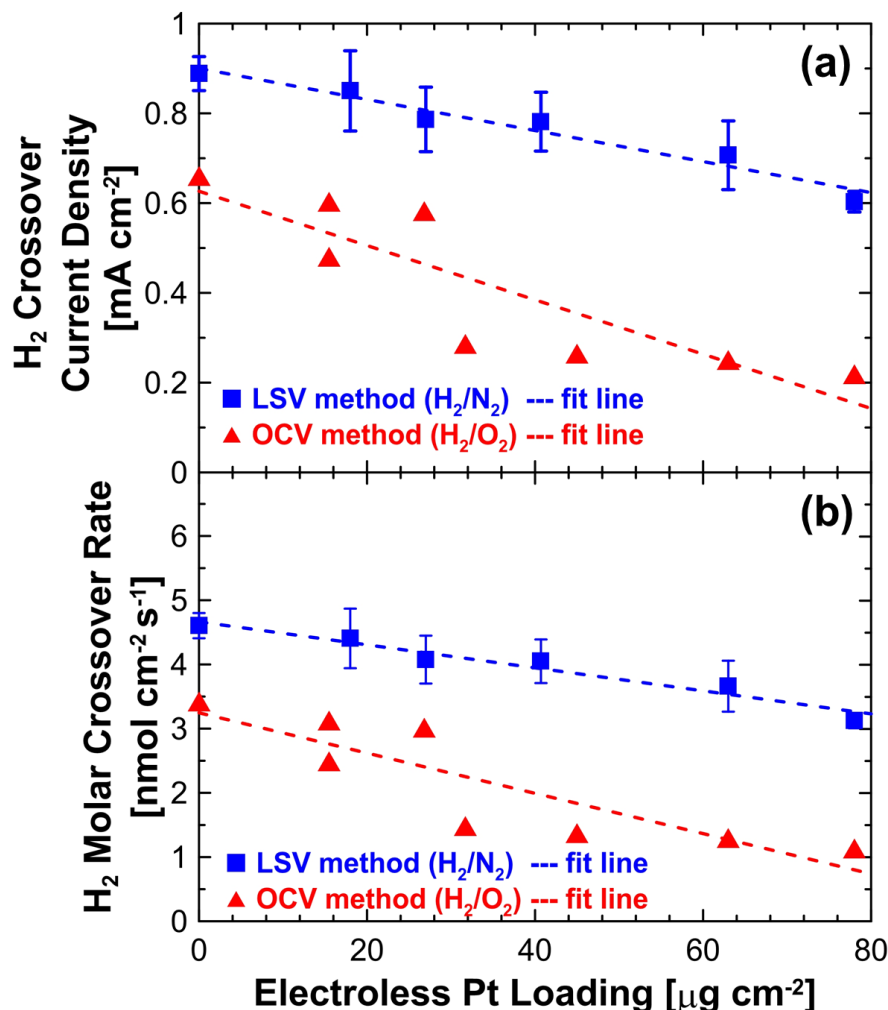
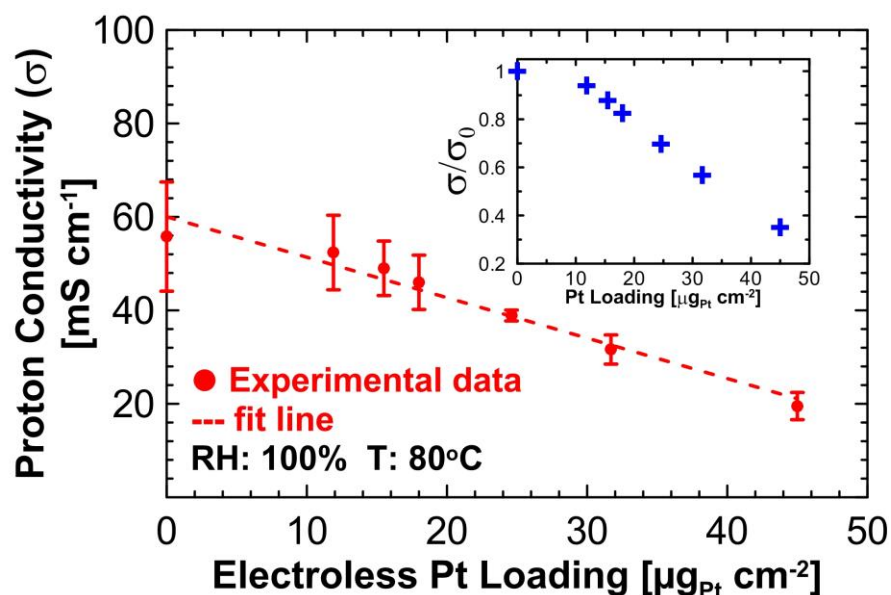


Figure 3.9: (a) Hydrogen crossover current density and (b) hydrogen crossover flux of MEAs with various electroless Pt loadings determined by LSV and OCV methods

### 3.9 Proton Conductivity and Exchange Current Density

In earlier discussion, it was indicated that the presence of an electroless Pt layer in the membrane can impede the transport of chemicals (e.g.,  $\text{NaBH}_4$ ) during synthesis and that of protons during fuel cell operation. Proton conductivity across the membrane is a critical aspect of the fuel cell performance and therefore needs to be elucidated. A decreased proton flux to the cathode catalyst layer leads to higher kinetic losses due to the lower concentration of protons involved in the ORR and higher ohmic losses due to increased ohmic resistance of the

membrane. Thus, it was important to study the effects of the electroless Pt layer loading on the kinetic parameters and membrane conductivity using ex-situ conductivity and O<sub>2</sub> polarization measurements under controlled humidity and temperature condition, respectively. Figure 3.10 shows the impact of Pt electroless loading on proton conductivity ( $\sigma$ ), as determined by ex-situ measurements. The measured proton conductivity of the 17  $\mu\text{m}$  thick JM membrane humidified at 100% RH and 80 °C was  $\sim 55 \text{ mS cm}^{-1}$ .



**Figure 3.10: Proton conductivity of membranes with different electroless Pt loadings determined by an ex-situ measurement. Inset: proton conductivity at specific Pt loading with respect to the proton conductivity of a bare membrane.**

This value is comparable to previously reported membrane proton conductivities (24 to 77  $\text{mS cm}^{-1}$ ) at 100% humidification at different temperatures as summarized in Table 3.3. The proton conductivity of the JM membrane decreases from  $\sim 55$  to  $\sim 20 \text{ mS cm}^{-1}$  as the Pt electroless loading increases from 0 to 45  $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . As shown by the TEM images in Figure 3.4, the density of the Pt layer in the membrane grows with increased electroless Pt loading and consequently the number of membrane channels available for proton transport is reduced. The

lower number of channels available for bulk proton diffusion (Grotthuss mechanism and diffusion in channels) leads to a drop in the proton conductivity. Figure 3.10 (inset) reveals that addition of a  $45 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  electroless Pt layer, which creates a dense band with a thickness of  $\sim 150 \text{ nm}$ , reduces the proton conductivity by  $\sim 60\%$ .

**Table 3.3. Summary of the reported proton conductivity of Nafion membranes and the JM membrane used in this work at fully humidified conditions**

| Membrane    | Thickness ( $\mu\text{m}$ ) | Temperature ( $^{\circ}\text{C}$ ) | $\sigma$ ( $\text{mS cm}^{-1}$ ) | Reference   |
|-------------|-----------------------------|------------------------------------|----------------------------------|-------------|
| JM membrane | 17                          | 80                                 | 55                               | this thesis |
| Nafion 112  | 60                          | 20                                 | 76                               | [115]       |
| Nafion 112  | 55                          | 90                                 | 37                               | [151]       |
| Nafion 112  | 51                          | 65                                 | 31                               | [152]       |
| Nafion 115  | 158                         | 20                                 | 75                               | [115]       |
| Nafion 115  | 127                         | 65                                 | 45                               | [152]       |
| Nafion 117  | 216                         | 20                                 | 77                               | [115]       |
| Nafion 117  | 220                         | $\sim 25$                          | 24                               | [153,154]   |
| Nafion 117  | -                           | 80-105                             | 50 - 60                          | [155]       |
| Nafion 117  | 183                         | 65                                 | 79                               | [152]       |
| Nafion 211  | 28                          | 20                                 | 59                               | [115]       |

Figure 3.11a shows IR-free oxygen polarization curves of half-MEAs with Pt electroless layers obtained with the half-cell set up. Loss of performance for the half-MEAs with increasing electroless Pt content can be observed, particularly when the loading exceeds a loading of  $40 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . To obtain the kinetic parameters from these  $\text{O}_2$  polarizations, two different approaches for fitting of the experimental polarization data from 0 to  $100 \text{ mA cm}^{-2}$  were used: i) two independent variables (i.e., Tafel slope and  $i_0$ ), and ii) one independent variable (i.e.,  $i_0$ ), and the results are summarized in Table 3.4. The latter approach implies that the Tafel slope was set constant for all samples. Both approaches show that the  $i_0$  generally decreases with increasing electroless Pt loading. The Tafel slope determined from the former method confirms that its deviations are relatively small (within 10%) with the variation of electroless Pt loading. This

minimum deviation was expected because the type and loading of the cathode catalyst used were unchanged for all samples. For subsequent analysis, we used the  $i_0$  values obtained by fitting the polarization curves with a fixed Tafel slope of  $-69 \text{ mV dec}^{-1}$  as shown in Figure 3.11b. Figure 3.11c shows the exchange current densities obtained by this Tafel analysis. Similarly, we observe a decrease in the exchange current density with the addition of electroless Pt particles. Here, the addition an electroless Pt layer with a loading of  $78.0 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  reduces the  $i_0$  by one order of magnitude (Figure 3.11c, inset).

The relationship between the exchange current density ( $i_0$ ) and the electroless Pt loading discussed earlier (Figure 3.11) allows us to elucidate the impact of the electroless Pt layer on the concentration of protons,  $[\text{H}^+]$ , at the membrane interface. According to its definition,  $i_0$ , denotes the rate of an electrochemical reaction (in this case the ORR) at equilibrium. Since reactants of the ORR are oxygen and protons,  $i_0$  can be mathematically expressed as:

$$i_0 = k \times P_{\text{O}_2}^a \times [\text{H}^+]^b \quad (3.16)$$

where  $k$  is the rate constant of the electrochemical reaction,  $P_{\text{O}_2}$  is the partial pressure of oxygen,  $[\text{H}^+]$  is the proton concentration, and  $a$  and  $b$  are the reaction orders for oxygen and  $[\text{H}^+]$ , respectively. Experimental values of the reaction order,  $b$ , with respect to the reaction conditions and catalyst types, have been reported previously. Damjanovic *et al.*, for instance, suggest reaction order values of 1.5 for protons  $[\text{H}^+]$  and 1 for  $P_{\text{O}_2}$  at low current densities, when excess  $\text{O}_2$ , an acidic environment and a platinum-based electrode are used (Equation (3.17)) [156,157].

$$i_0 = k \times P_{\text{O}_2} \times [\text{H}^+]^{1.5} \quad (3.17)$$

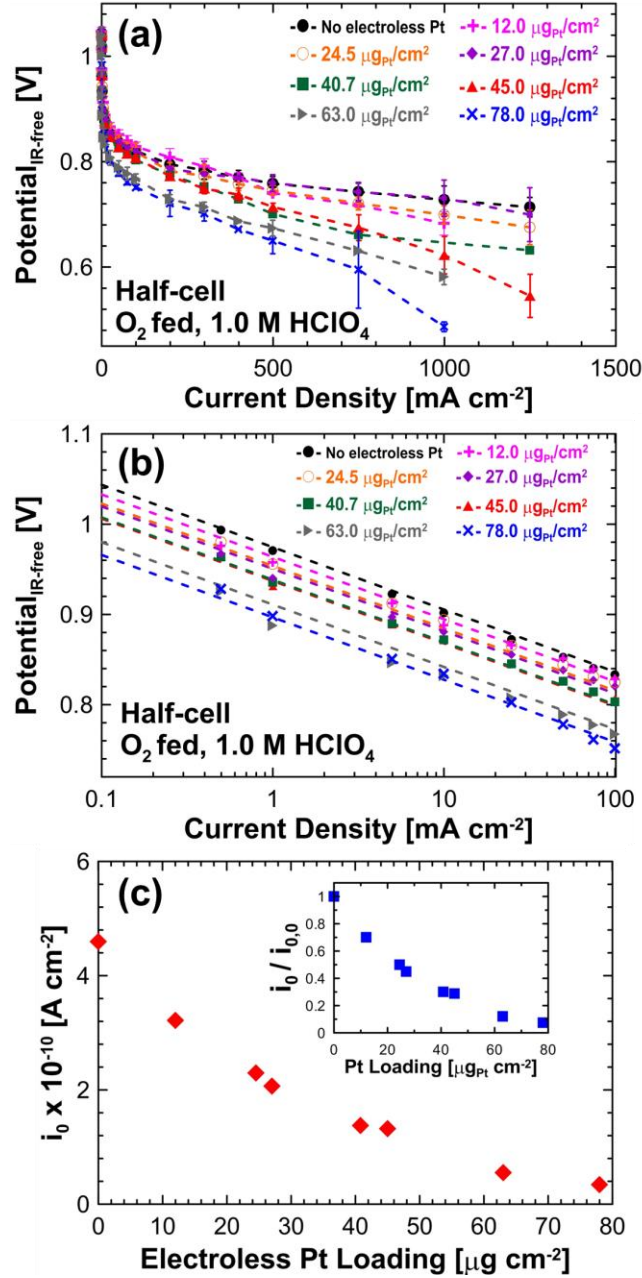


Figure 3.11: (a) Polarization curves of half-MEAs with different Pt loadings conducted in a half-cell, (b) correlation between electroless Pt loading and kinetic performance (0-100 mA cm<sup>-2</sup>) plotted on a logarithmic scale, and (c) exchange current density derived from Tafel analysis vs. Pt electroless loading. Inset: the value of exchange current density relative to the exchange current density of the baseline bare membrane vs. electroless Pt loading.

**Table 3.4. Kinetic parameters from fitting of half-cell polarization curves (0 – 100 mA cm<sup>-2</sup>) with two and one independent variable fitting approaches**

| Loading<br>(mg <sub>Pt</sub> cm <sup>-2</sup> ) | Two Independent Variable Fitting                                             |                                        | One Independent Variable Fitting                                          |                                        |
|-------------------------------------------------|------------------------------------------------------------------------------|----------------------------------------|---------------------------------------------------------------------------|----------------------------------------|
|                                                 | Exchange Current Density <sup>a</sup><br>(A cm <sup>-2</sup> <sub>Pt</sub> ) | Tafel Slope<br>(mV dec <sup>-1</sup> ) | Exchange Current Density <sup>a</sup> (A cm <sup>-2</sup> <sub>Pt</sub> ) | Tafel Slope<br>(mV dec <sup>-1</sup> ) |
| 0                                               | $4.6 \times 10^{-10}$                                                        | 69                                     | $(4.6 \pm 0.3) \times 10^{-10}$                                           | 69                                     |
| 12.0                                            | $1.2 \times 10^{-10}$                                                        | 64                                     | $(3.2 \pm 0.3) \times 10^{-10}$                                           | 69                                     |
| 24.5                                            | $2.1 \times 10^{-10}$                                                        | 67                                     | $(2.7 \pm 0.2) \times 10^{-10}$                                           | 69                                     |
| 27.0                                            | $6.0 \times 10^{-11}$                                                        | 62                                     | $(2.1 \pm 0.4) \times 10^{-10}$                                           | 69                                     |
| 40.8                                            | $1.1 \times 10^{-10}$                                                        | 67                                     | $(1.4 \pm 0.2) \times 10^{-10}$                                           | 69                                     |
| 45.0                                            | $8.1 \times 10^{-11}$                                                        | 66                                     | $(1.3 \pm 0.3) \times 10^{-10}$                                           | 69                                     |
| 63.0                                            | $1.9 \times 10^{-11}$                                                        | 65                                     | $(5.5 \pm 2.0) \times 10^{-11}$                                           | 69                                     |
| 78.0                                            | $1.0 \times 10^{-10}$                                                        | 75                                     | $(3.4 \times 10^{-11})$                                                   | 69                                     |

<sup>a</sup> the exchange current density is normalized to the Pt surface area. The ECSA is taken as 29 m<sup>2</sup> g<sup>-1</sup><sub>Pt</sub> as determined in ref [158].

Error bars represent 95% of the confidence of the fitting parameters

In our work, oxygen was delivered to the cell at 100 kPa and at a constant flow rate of ~70 SCCM or a cathode stoichiometry equivalent to 10 at 1000 mA cm<sup>-2</sup>. As the oxygen feed to the electrode was in excess, the effect of the P<sub>O<sub>2</sub></sub> change on i<sub>0</sub>, due to oxygen consumption, was assumed to be negligible. The impact of the [H<sup>+</sup>] on the i<sub>0</sub> can then be expressed by:

$$i_0 = k' \times [H^+]^b \quad (3.18)$$

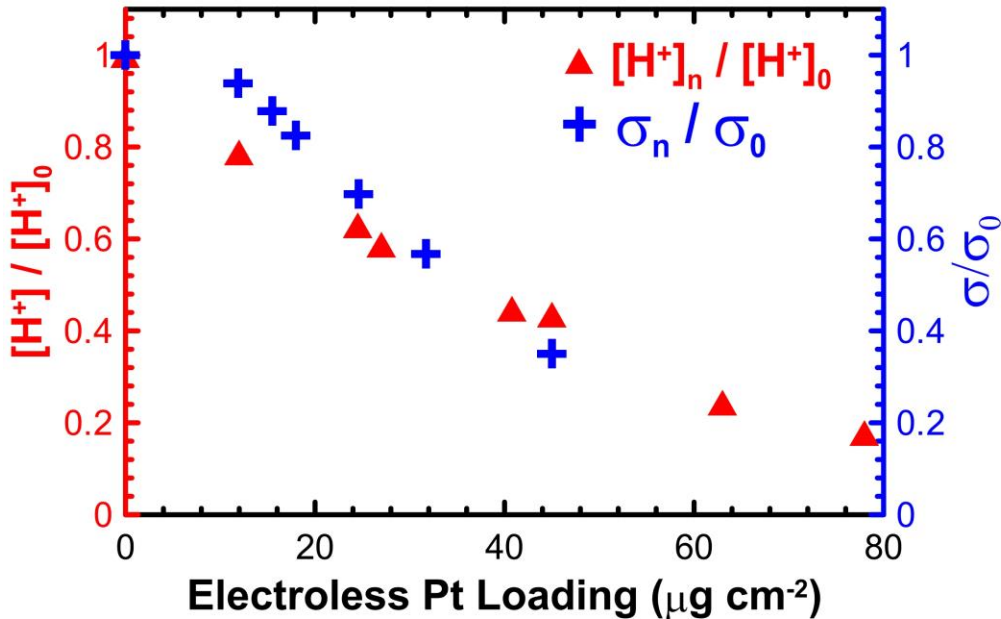
or using a value of 1.5 for the proton's reaction order b, which leads to:

$$i_0 = k' \times [H^+]^{1.5} \quad (3.19)$$

Therefore, the ratio between i<sub>0</sub> of a sample with a loading of n (μg cm<sup>-2</sup>) electroless Pt and the baseline (no electroless Pt) can be expressed by:

$$\frac{(i_0)_n}{(i_0)_0} = \left( \frac{[H^+]_n}{[H^+]_0} \right)^{1.5} \quad (3.20)$$

where  $(i_0)_n/(i_0)_0$  and  $[H^+]_n/[H^+]_0$  are the ratios of exchange current density and proton concentration of the MEAs with electroless Pt loading of  $n$  ( $\mu\text{g cm}^{-2}$ ) to the corresponding quantities with no electroless Pt loading, respectively. Equation ((3.20) was then used to translate the data in the inset of Figure 3.11 ( $i_0$  vs electroless Pt loading) into a new plot showing the relationship of  $[H^+]$  vs. the electroless Pt loading. Figure 3.12 compares the resulting relationship between  $[H^+]$  vs. Pt loading and proton conductivity ( $\sigma$ ) vs. electroless Pt loading adopted from Figure 3.11. It is evident that the presence of the electroless Pt loading has a similar impact on the proton concentration at the membrane and catalyst layer interface and conductivity of the protons. For example, with loadings of 31 and 45  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ , we calculate the reduction of proton concentration at the interface and proton conductivity across the membrane to be about in the range of 35-40% and 60-65%, respectively.



**Figure 3.12: Impact of Pt electroless loading to the decrease in proton concentration  $[H^+]$  in the catalyst layer derived from polarization and proton conductivity ( $\sigma$ ) measured ex-situ.**

### 3.10 Fuel Cell Performance

#### 3.10.1 Polarization Curves at Wet and Dry Conditions

MEAs with different electroless Pt loadings were tested in a single cell with controlled humidity, flow rate, and temperature to investigate the impact of the electroless Pt layer on the performance. Parallel channel flow fields were used at the cathode and anode with a high stoichiometry of air feed in the cathode flow field to minimize the mass transport losses caused by oxygen concentration and diffusion, and water flooding, i.e., quasi 1D testing. With these provisions, the fuel cell performance (in this case with the presence of an electroless Pt layer) can be simplified as a function of proton flux, membrane conductivity (or resistance), and the membrane hydration level. To improve the operational flexibility of PEMFCs with respect to the humidity level, it is critical to recognize the trade-offs between the improved membrane hydration and the reduced proton conductivity under various humidity levels when the electroless Pt layer is used in the membrane. This analysis would lead to an optimum electroless Pt loading in the membrane.

**Table 3.5. Normalized high frequency resistance (HFR) values of the baseline MEA and MEAs with various electroless Pt loadings (at 100% and 30% RH conditions) measured in-situ during the fuel cell polarization measurements**

| Electroless Pt Loading ( $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ) | 100% RH                                                              |                                                                      | 30%RH                                                                |                                                                      |
|----------------------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------------------------------|
|                                                                      | HFR at Polarization 1 ( $\text{m}\Omega \text{ cm}^2$ ) <sup>a</sup> | HFR at Polarization 4 ( $\text{m}\Omega \text{ cm}^2$ ) <sup>a</sup> | HFR at Polarization 1 ( $\text{m}\Omega \text{ cm}^2$ ) <sup>a</sup> | HFR at Polarization 3 ( $\text{m}\Omega \text{ cm}^2$ ) <sup>a</sup> |
| 0                                                                    | 83 ± 13                                                              | 85 ± 14                                                              | 206 ± 13                                                             | 399 ± 15                                                             |
| 12.9                                                                 | 93 ± 14                                                              | 88 ± 10                                                              | 126 ± 10                                                             | 225 ± 19                                                             |
| 16.7                                                                 | 105 ± 14                                                             | 94 ± 12                                                              | 171 ± 18                                                             | 184 ± 4                                                              |
| 21.1                                                                 | 81 ± 19                                                              | 95 ± 13                                                              | 229 ± 20                                                             | 234 ± 25                                                             |
| 45.0                                                                 | 115 ± 13                                                             | 109 ± 14                                                             | 196 ± 21                                                             | 320 ± 25                                                             |

<sup>a</sup> the values reported are average values of the HFR measurements over five different distinct points across the ohmic region of the respective polarization curve (i.e., 300 – 1000  $\text{mA cm}^{-2}$  for 100% RH and 200 – 500  $\text{mA cm}^{-2}$  for 30% RH) with the error bar representing the standard deviation of the measured points from three different samples.



Figure 3.13a-d shows the average values and standard deviations of cell potentials at specific current densities for the baseline MEAs (i.e., no electroless Pt layer) and with different loading of electroless Pt layer. The standard deviations of all the polarization points were smaller than 20 mV, indicating that repeatable and consistent measurements were obtained with baseline samples and over the time span of multiple polarization experiments. All the MEAs were subjected to a conditioning step of constant current ( $500 \text{ mA cm}^{-2}$ ) operation for a minimum period of 12 h, and subsequently four consecutive polarization cycles performed at 100% RH. The negligible differences in the polarization measurements observed between the first (Figure 3.13a) and the fourth (Figure 3.13b) sets of polarization data show that the MEA performances were quite stable during the wet polarization cycles and that adequate conditioning had been performed. At 100% RH, Figure 3.13a and b show that the MEAs with an electroless Pt layer loading of  $\leq 16.7 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  have an equivalent performance to the baseline (i.e., no electroless Pt layer). These results indicate that below an electroless Pt loading of  $20 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ , no significant performance losses are imposed by the electroless Pt layer. However, the potential losses become noticeable when the electroless Pt layer loadings exceed  $20 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  and increase with the electroless Pt loading, similar to the data reported in Figure 3.10. The agreement between half-cell and single cell results confirms that the presence of thicker electroless Pt layers ( $>20 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ) impedes the conduction of protons across the membrane; hence, leading to a reduced concentration of protons near the membrane/catalyst layer interface and reduced kinetic performance of the MEAs. The potential drops become more pronounced with higher electroless Pt loadings. For example, at an operating current density of  $1000 \text{ mA cm}^{-2}$ , cell potentials of  $\sim 0.47$  and  $\sim 0.43$  V were achieved with the presence of  $21.1$  and  $45.0 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  electroless Pt

layer loading in the membranes. These potentials correspond to 30 and 70 mV potential drops with respect to the baseline potential of  $\sim 0.5$  V at  $1000 \text{ mA cm}^{-2}$ , respectively (Figure 3.13a).

HFR measurements at 100% RH are summarized in Table 3.5. These measurements show that the ohmic resistance of the MEAs increases with the electroless Pt loading and confirms the ex-situ proton conductivity measurements shown in Figure 3.10. Addition of a  $45 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  electroless Pt layer, for instance, increases the average HFR value of the MEA from  $\sim 83$  to  $\sim 115 \text{ m}\Omega \text{ cm}^2$ , during the first polarization, and from  $\sim 85$  to  $\sim 109 \text{ m}\Omega \text{ cm}^2$ , during the fourth polarization.

After the wet condition (100% RH) polarization measurements, the MEAs were subjected to a dry conditioning step (30% RH) and were held at a current density of  $500 \text{ mA cm}^{-2}$  at a cathode stoichiometry of 10 for 1 h to purge the remaining humid air in the humidifier, lines, and cell. After this low humidity conditioning step, the polarization measurements of all MEA samples shows performance losses (Figure 3.13c), and the values of HFR shows an increase in the resistance (Table 3.5). The HFR of the baseline MEA, for instance, increased by more than twofold, from  $\sim 85 \text{ m}\Omega \text{ cm}^2$  (under wet conditions) to  $\sim 205 \text{ m}\Omega \text{ cm}^2$  (after conditioning). In addition, it can be observed that the averaged performance of the baseline MEAs in the 1<sup>st</sup> polarization dropped more than that of the other MEAs, particularly those with electroless Pt loadings less than  $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  (Figure 3.13c). This contrasted with the wet condition (100% RH) polarizations, where the performances of the baseline and the MEAs with electroless Pt loadings less than  $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  were almost identical (Figure 3.13a and b). At  $500 \text{ mA cm}^{-2}$ , for instance, the cell potentials of the MEAs with a  $16.7 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  and  $12.9 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  electroless Pt layer were 80 and 69 mV higher than that of the baseline respectively, (Figure 3.13c). Table 3.5 also shows that the MEAs with electroless Pt loadings less than  $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  have a lower HFR compared to

the baseline, indicating a better hydration of the MEA. As discussed earlier, the recombination of hydrogen and oxygen due to the presence of the electroless Pt layer, which is evidenced by the reduced hydrogen crossover current, results in production of water in the membrane subsurface. The water produced in the membrane subsurface causes improved hydration of the membrane indicated by the lower values of HFR. The improved hydration of the membranes in the MEAs with electroless Pt loadings less than  $20 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  led to smaller loss of performance at low humidity conditions. On the other hand, MEAs with electroless Pt layers thicker than  $20 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  had lower performance at any current density compared to the ones with a thinner electroless Pt layer. For these MEAs, the diminishing gain from the improved membrane hydration by the electroless Pt layer was offset by a more pronounced reduction of proton conductivity.

Figure 3.13d shows a further reduction of the performance because of accelerated drying after several polarization cycles. After two additional and consecutive polarization cycles, drier membrane conditions were experienced as indicated by a lower cell potential and higher HFR. At  $500 \text{ mA cm}^{-2}$ , for example, the averaged baseline MEA potential dropped by  $\sim 90 \text{ mV}$ , from  $\sim 0.42$  during the first polarization to  $\sim 0.33 \text{ V}$  in the third polarization (Figure 3.13c and d). Similarly, the HFR values increase by almost two-folds, from  $\sim 200$  to  $378 \text{ m}\Omega \text{ cm}^2$  (Table 3.5). During this third polarization cycle, MEAs with an additional of electroless Pt layer loadings less than  $21.1 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  show a significant potential difference than the baseline MEA, particularly at higher current densities ( $>500 \text{ mA cm}^{-2}$ ). Given that the MEA resistances of those MEAs were also lower than those of the baseline, one can conclude that the benefits observed by the MEAs with low loading electroless Pt were resulted from the improved proton conduction due to a better hydration. Because of the limitations in the proton conductivity, MEAs with higher loadings of electroless Pt layers (e.g.,  $45 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ) do not show this performance gain (Figure

3.13d), which is also manifested by a higher value of HFR (Table 3.5). From all these measurements, it is clear that the electroless Pt layer improves the rehydration ability of the MEAs, but due to the negatively competing effect of proton conductivity, imposed by a thick Pt layer, the loading should be no more than about  $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  in the cathodic side of the membrane subsurface. This structure can be synthesized by using the non-equilibrium impregnation reduction method with the conditions explained in Section 2.1 and a reduction time of less than 5 minutes.

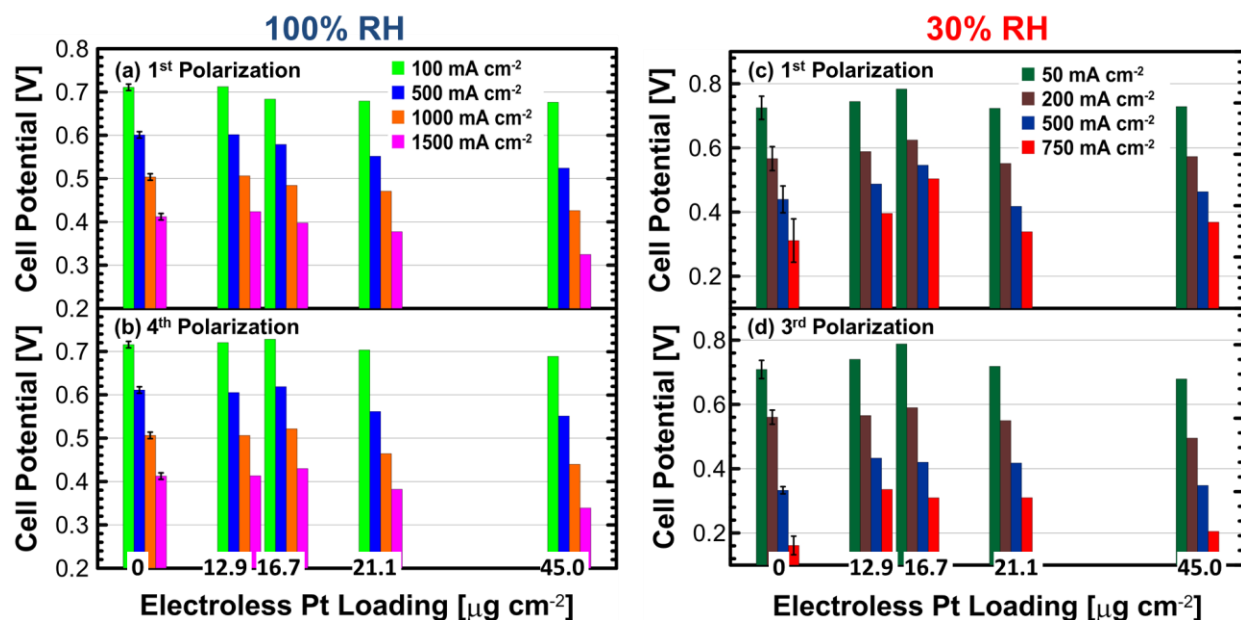
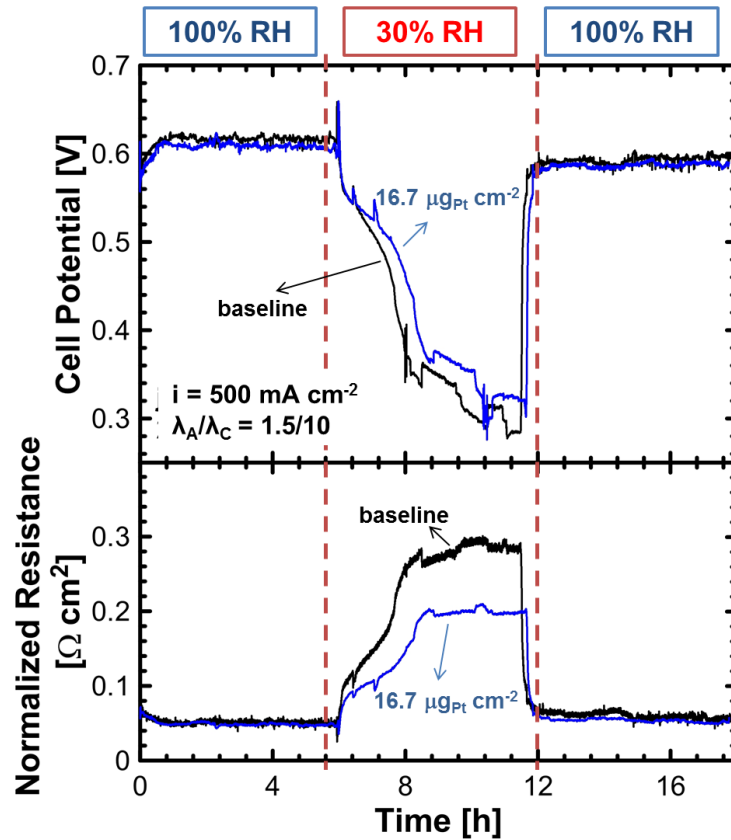


Figure 3.13: Effect of electroless Pt loading on the (a) first and (b) fourth polarization curves performed at 100% RH, and (c) first and (d) third polarization curves performed at 30% RH at various current densities.

### 3.10.2 Humidity Cycling Test

In addition to the polarization tests, a longer humidity cycling test (high/low/high humidity; 6 hours each) was performed to further evaluate the long-term performance and durability of the electroless Pt layer. Figure 3.14 shows a comparison of the performance of the baseline MEA and the MEA with a  $16.7 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . During the prolonged (6 h) drying step, the

MEA with a  $16.7 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  electroless Pt layer consistently shows a higher cell potential and about 30% lower HFR ( $200 \text{ vs. } 300 \text{ m}\Omega \text{ cm}^2$ ) compared to those of the baseline MEA. This indicates that membrane hydration levels in the presence of electroless Pt layer remain higher during this continuous operation. The optimum performance was achieved by the MEAs with a loading of  $16.7 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  electroless Pt layer in the membrane subsurface. Pt electroless layers with a loading  $<20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  have negligible impact under wet conditions but demonstrate a better performance under low humidity conditions, and as such these enhanced MEAs certainly deserve further investigation and development.



**Figure 3.14:** Cell potential and resistance profiles of a GDE-based MEA with additional  $16.7 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  Pt electroless layer and a baseline under relative humidity cycle test.

### 3.11 Conclusions

A controlled synthesis of platinized Nafion membranes with Pt loadings  $<80 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  was successfully demonstrated using a non-equilibrium impregnation and reduction method. Deposition of Pt yielded the formation of dense and thin Pt layers ( $<250 \text{ nm}$ ) with a homogeneous lateral (surface) distribution of grains in one side of the membrane subsurface. The density of Pt layers appeared to be increased with loading suggesting a better inter-particle connectivity. Simple geometric-based models derived from XRD and ECSA were used to describe the growth mechanism of Pt in the layer (assuming spherical shape of Pt particle). For the loading range studied ( $<80 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ), increased trends in the measured values of Pt grain size and also the ECSA indicate that both grain growth and increased connectivity or Pt utilization occur as Pt loading increases. This also reveals that the increase in loading is attributed to both crystallite size growth and coalescence of smaller Pt particles (Appendix 5.2B.4). The increase in Pt utilization was determined in terms of the grain size, i.e.,  $\propto r_{\text{Pt-grain}}^{1.80}$ . Rapid increase in the in-plane electronic conductivity and a simultaneous increase in the optical reflectivity of the samples for loadings greater than  $32.0 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  showed that coalescence of Pt grains occurs in addition to the grain growth.

Application of the low-loading electrolessly deposited Pt layer ( $<80 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ) in the ionomer membrane subsurface for enhanced operation of hydrogen fuel cells was also thoroughly investigated. LSV and OCV methods showed that at open circuit operation, reduction of the hydrogen crossover current was proportional to the loading of the electroless Pt layer. The presence of a  $78 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  electroless Pt layer showed up to 65% reduction of the  $\text{H}_2$  crossover current. The exchange current density and the proton concentration involved in the ORR

decreases as the electroless Pt loading increases. Similarly, the proton conductivity ( $\sigma$ ) of the electrolessly deposited Pt membrane appears to be inversely proportional to the loading of the Pt layer embedded in its subsurface. Fuel cell tests at controlled humidity and temperature were used to investigate the benefit of membrane rehydration imposed by the electroless Pt layer under low humidity conditions and the competing effects of the reduced proton flux on the overall performance. The performance of the GDE-based MEAs with the electroless Pt layer tested with a quasi 1D parallel cell demonstrates a clear benefit of the electroless Pt with loadings  $<20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . MEAs with such a low electroless Pt loading have a comparable performance to the baseline and yet improved the performance at low humidity conditions due to a better humidification of the membrane. The initial durability test for the low loading electroless Pt was performed with an 18 h continuous humidity cycling operation. The electroless Pt layer showed a higher potential and a lower resistance in the dry period and equivalent performance in the wet periods. This performance gain with the addition of low loading electroless Pt is beneficial for the MEA assembled with GDE-method, where the gaps between cathode catalyst layer and membrane are likely to exist.

## Chapter 4: Catalyst Layer | Microporous Layer Interface<sup>3</sup>

### 4.1 Introduction

In this chapter, a new fabrication method in which a hydrophobic, PTFE-mixed MPL is applied directly on the CCM to reduce the CCL|MPL gaps was introduced, and the performance of the MEAs with this ‘modified MPL’ were thoroughly investigated and optimized. By eliminating the CCL|MPL interfacial gaps, the modified MPL supposedly results in an increase in fuel cell performance particularly at higher humidity conditions with a thinner CL. The CCMs used in this study were a low Pt loading CCM manufactured by Johnson Matthey consisting of a cathode catalyst loading of  $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  (thickness of  $\sim 3 \text{ }\mu\text{m}$ ), anode catalyst with a loading of  $0.04 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ , and a reinforced cation exchange membrane with a thickness of  $17 \text{ }\mu\text{m}$ . The total Pt loading of the electrodes (i.e.,  $0.14 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ) is close to the DOE 2020 target of  $0.125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ , which is becoming the future benchmark. The content of the PTFE as hydrophobic agent in the modified MPL used in this study was set constant at 20% wt. This PTFE loading has shown the optimum performance considering two competing factors affected, namely, membrane hydration and mass transport loss [94,95].

In this study, the first set of experiments was conducted to demonstrate the benefit of having a modified MPL with different MEA architectures. Four different types of MEA architectures (Figure 4.1) were assembled: (i) MEA without MPL, (ii) MEA with only commercial MPL, (iii) MEA with modified MPL applied only on the CCL, and (iv) MEA with

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<sup>3</sup> Sections of this work have been published in:

Daniel, L.; Bonakdarpour, A.; Sharman, J.; Wilkinson, D. P. “New CCL|MPL Architecture Reducing Interfacial Gaps and Enhancing PEM Fuel Cell Performance.” *Fuel Cells*. **2020**, 2, 224-228

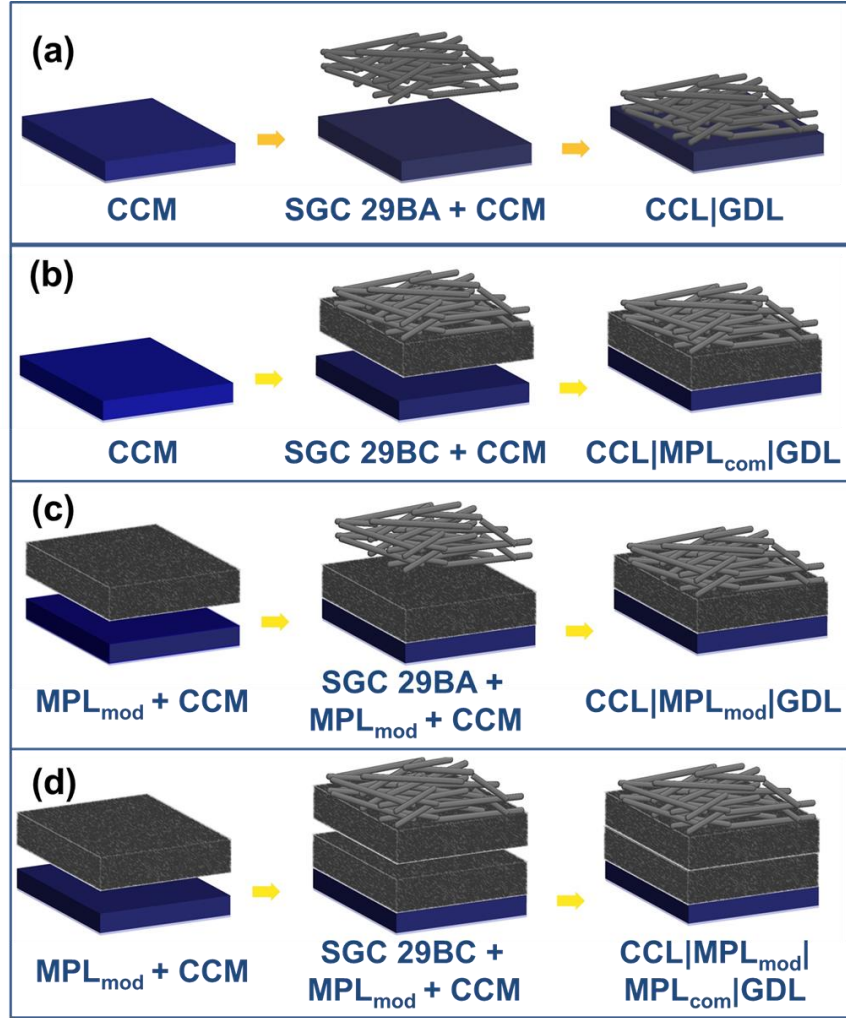
Sections of this work have been prepared as:

Daniel, L.; Bonakdarpour, A.; Govindarajan, R.; Wilkinson, D. P. “Modified CCL|MPL Interfacial Structure for Improved Low Pt Loading PEM Fuel Cell Performances” (in preparation)



both commercial and modified MPLs. All samples then were combined with an SGC 29BC as the anode diffusion media to complete the MEA structure. For testing, an MEA with a masked active area of  $14\text{ cm}^2$  ( $7\text{ cm} \times 2\text{ cm}$ ) was placed in a TP50 cell (100 psi compression). The humidity and pressure of the gases were maintained at 100% and 150 kPag, respectively, and the cell was operated at  $80^\circ\text{C}$ . All MEAs were conditioned for six hours ( $80^\circ\text{C}$ ,  $500\text{ mA cm}^{-2}$ ). In order to test the repeatability, three different baseline MEA samples (Figure 4.1b) were fabricated and tested (at the beginning, middle, and end of the testing period). Likewise, two MEA samples with modified and commercial MPLs (Figure 4.1d) were fabricated and tested. Here, Vulcan XC72R was used as the MPL carbon material. The average polarization curves are reported with the error bars representing the standard deviation obtained. The results of this set of experiments will be discussed in Sections 4.4.

The second set of experiments were conducted to find the best performing MPL material (carbon black type) and loading as well as the effect of the carbon morphology to the performance under different testing conditions. The MEA architecture shown in Figure 4.1d is used for MEA assembly in this study. Three carbon types, namely Acetylene Black (AB), Black Pearl 2000 (BP), and Vulcan XC-72R (VC) were used as the MPL materials, and a pair of Sigracet 29BC carbon papers was used as a gas diffusion media on both the anode and cathode sides to complete the MEA. Detailed information on the sample synthesis and preparation and testing procedure are explained in Sections 2.1 and 2.4. The results obtained from the second set of experiments were discussed in Sections 4.5 - 4.7.



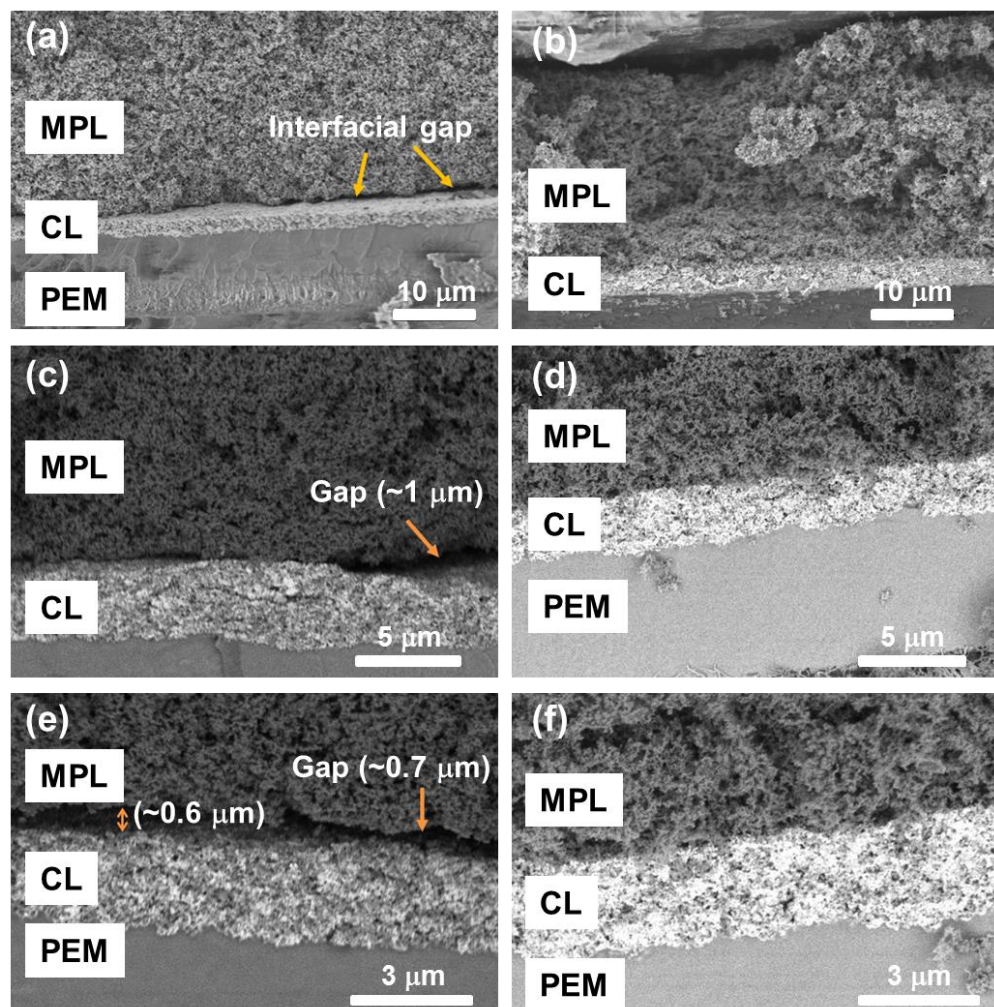
**Figure 4.1: Schematics of the different MEA architectures: (a). MEA without MPL, (b) MEA with commercial MPL, (c) MEA with modified MPL on CCM, and (d). MEA with double MPLs.**

## 4.2 Modified MPL and Interfacial Gaps

As discussed in Section 1.5.4, the conventional MPL synthesis method yields interfacial gaps at the CCL|MPL interface which potentially cause performance degradation at high current densities. The approach taken in this work was to eliminate the gaps by coating the MPL directly on the CCL. By far, the hindering factor of applying a hydrophobic, PTFE mixed MPL directly on the CCL is the high temperature needed for the PTFE sintering process (i.e.,  $>200^{\circ}\text{C}$ ), which

causes irreversible damage to the Nafion membrane. Here, a low sintering temperature PTFE was used as the hydrophobic agent to enable the MPL sintering with a CCM.

The microscopic structure of the CCL-modified MPL was then examined with SEM and compared to the conventional structure of CCL-MPL. SEM images of the MPL|CCL interfaces fabricated with the conventional method (Figure 4.2a, c, and e) clearly show noticeable gaps of up to 1  $\mu\text{m}$  even after 100 psi compression. The presence of these gaps leads to a non-uniform and disconnected interface region. The majority of the non-mating surface roughness between the CCL and the MPL results in interfacial gaps which can be filled by liquid water during higher current density operation. This observation is in agreement with previous reports which show that the interfacial gaps are dictated by the difference of the surface contours, especially the MPL [101,109,159]. On the other hand, the application of the modified-MPL on the CCL results in negligible interfacial gaps since the MPL surface contour follows the contour of the catalyst layer (Figure 4.2b, d, and f).

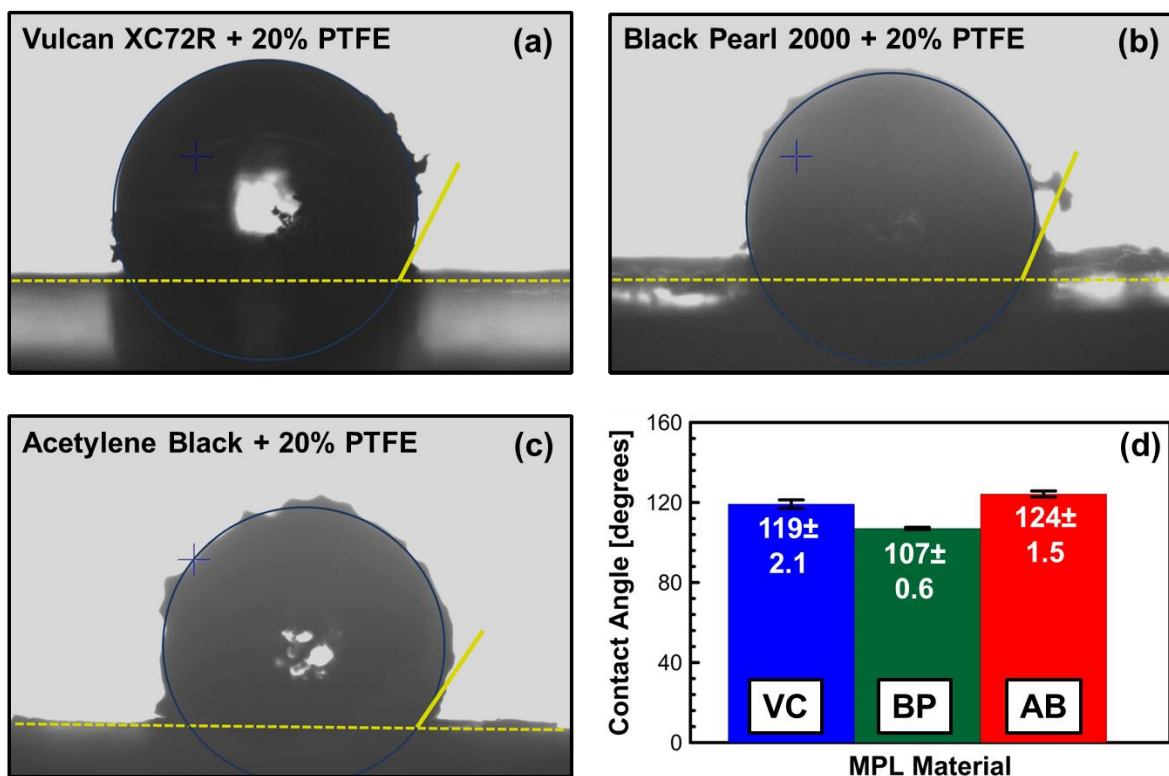


**Figure 4.2: SEM images of CCL|MPL interfaces of (a), (c), and (e) commercial MPL and CCM with gaps even after 100 psi compression; (b), (d), and (f) MPL applied on CCM with eliminated gaps.**

### 4.3 Wettability of MPL

Surface wettability of all *modified MPL* materials (Acetylene Black, Black Pearl 2000, and Vulcan XC72R) were examined by static contact angle measurements at room temperature (i.e., 22°C) and water immersion tests at both room temperature and PEMFC operating temperature (i.e., 80°C), respectively. Results of these measurements show that all MPL materials with 20% Teflon AF 1600 content are hydrophobic as indicated by both static contact angle measurements (Figure 4.3) and water immersion tests (Figure 4.4). The hydrophobicity of all MPL samples

synthesized with Teflon AF 1600 in the mixture suggests that the PTFE is mixed and distributed evenly in the layer. It is critical to produce a hydrophobic MPL|CCL interface to have proper water management because hydrophilic MPLs have shown an inferior performance under high humidity operating conditions [97]. To determine the wettability behavior upon heating, i.e., simulating the water-MPL interactions of an operating PEMFC, immersion tests of all MPL materials were conducted at room (22°C) and fuel cell temperatures (80°C), respectively. Figure 4.4 shows that at 22°C all the MPL material aggregates float on the water surface, confirming the hydrophobic nature of these MPL materials. However, small fractions of BP- and VC-based MPL aggregates sink after being heated to 80°C, while no changes were observed for AB-based MPL aggregates. The higher water adsorption in the pores of BP- and VC-based MPL materials, particularly at higher temperatures, could be attributed to their higher porosity (Table 4.1) and different surface functionality due to different production processes. Acetylene black is produced from heating acetylene ( $C_2H_2$ ) gas in the absence of air [160]. This production process yields a carbon black with high carbon purity (>99%), less oxygenated moieties, and lower surface area [161]. These properties are commonly found in carbon blacks produced by Thermal Black processes, i.e., heating low molecular weight hydrocarbon in an inert atmosphere [162]. On the other hand, Vulcan XC-72R and Black Pearl are categorized as Furnace Black type, which means they are produced from partial combustion of aromatic oils [161]. This production process results in carbons with higher surface area and oxygenated functional groups. The more hydrophilic nature of BP and VC is attributed to the high surface area and surface oxides formed during the production and storage stages [163,164].



**Figure 4.3:** Static contact angle measurements of treated a) Vulcan XC-72R, b) Black Pearl 2000, and c) Acetylene Black. d) Average static contact angle of the VC-, BP-, and AB-based MPLs measured from three different spots on the same sample for each type of carbon material used.

**Table 4.1. Pore and particle size characterizations of various MPL carbon black types used in the modified MPL study**

| Carbon Type       | $S_{\text{BET}}^{\text{a}}$<br>( $\text{m}^2 \text{g}^{-1}$ ) | $V_{\text{micro}}^{\text{b}}$<br>( $\text{cm}^3 \text{g}^{-1}$ ) | $V_{\text{total}}^{\text{c}}$<br>( $\text{cm}^3 \text{g}^{-1}$ ) | Particle Size <sup>d</sup><br>(nm) |
|-------------------|---------------------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|------------------------------------|
| Black Pearls 2000 | 1509                                                          | 0.278                                                            | 2.586                                                            | 15                                 |
| Vulcan XC72R      | 234                                                           | 0.032                                                            | 0.478                                                            | 50                                 |
| Acetylene Black   | 60                                                            | 0.012                                                            | 0.169                                                            | 42                                 |

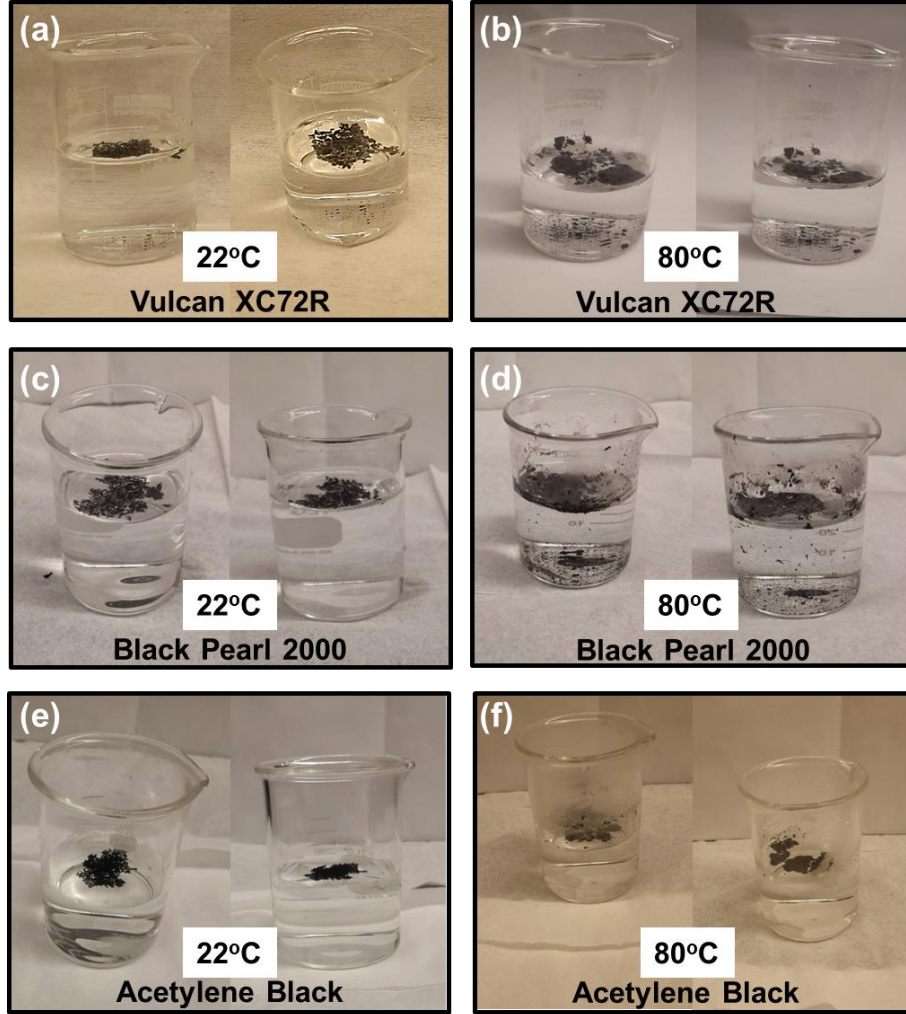
<sup>a</sup> Determined from the normalized partial pressure ( $P/P_0$ ) range of  $0.05 < P/P_0 < 0.3$  (data provided by Rubenthiran Govindarajan)

<sup>b</sup> Obtained from the t-plot method (data provided by Rubenthiran Govindarajan)

<sup>c</sup> Determined with the total gas adsorbed at  $P/P_0 = 0.99$  (data provided by Rubenthiran Govindarajan)

<sup>d</sup> Values obtained from Kinoshita [165]





**Figure 4.4:** Photographs of the immersion test results of the aggregates of the treated MPLs used in this study: (a) Vulcan XC-72R in 22°C water, (b) Vulcan XC-72R in 80°C water, (c) Black Pearl 2000 in 22°C water, (d) Black Pearl 2000 in 80°C water, (e) Acetylene Black in 22°C water, and (f) Acetylene Black in 80°C water.

#### 4.4 Effect of the Presence of Modified MPL

The first set of polarization curves and their corresponding resistances show the effect of the presence of a commercial MPL (MPL<sub>com</sub>) and modified MPL (MPL<sub>mod</sub>) as well as the combined MPLs on the fuel cell performance. Figure 4.5b shows that the presence of a commercial MPL deposited to the gas diffusion layer (GDL) as illustrated in Figure 4.1b reduces the MEA resistance from  $\sim 90$  to  $\sim 65$  mΩ cm<sup>2</sup> from the MEA without any MPL illustrated in

Figure 4.1a. This is also reflected in a better overall polarization performance as indicated by a higher polarization curve of the MEA with conventional MPL (black line) compared to the one without any MPL (red line) in Figure 4.5a. The reduction in resistance is due to increased contact points provided by the CCL|MPL<sub>com</sub> interface than that of the CCL|GDL interface. The comparison between MEAs with a modified MPL only (0.8 mg<sub>VC</sub> cm<sup>-2</sup> or 20 μm equivalent thickness) and commercial MPL only in Figure 4.5a also reveals that the MEA with a modified MPL outperforms the MEA with a commercial MPL in high current density region (>1000 mA cm<sup>-2</sup>) where the mass transport loss due to flooding is intensified. This indicates that the modified MPL coated on the CCL reduces water flooding at the CCL|MPL interface to mitigate flooding in the vicinity of the CCL [103]. On the other hand, two MEA samples (duplicate measurement) consisting of a 0.8 mg<sub>VC</sub> cm<sup>-2</sup> modified MPL on the CCL and commercial MPL (Figure 4.1d), were tested and the averaged polarization plots show even a higher performance gain at high current density region under wet conditions. This combined MPL architecture also further minimizes ohmic losses from ~65 to ~45 mΩ cm<sup>2</sup> showing an improved physical contact between layers in the MEA [105,108]. With this combined MPL architecture, the interfacial gaps may occur between the first and the second MPLs; however, as indicated by the lower through plane resistance than the baseline, these gaps have less effect than gaps between the CCL and MPL. The closer roughness between the two MPLs results in a better contact between those layers. The higher performance in the mass transport region also shows that the gaps occurring between the two MPLs yield less flooding in the MEA than those between the CCL and MPL, presumably due to the more hydrophobic nature of both MPLs and the location of the gaps that are farther from the CCL. Despite the advantages of achieving a higher current density shown by having only a modified MPL in the MEA, the presence of the thicker existing MPL coated on the



GDL is still beneficial to provide mechanical strength and protect the CCM from the carbon fibers intrusion from the GDL [77,78].

Tests under  $\text{H}_2/\text{O}_2$  were performed to examine the kinetic effect of having an extra MPL layer attached to the CCL. Figure 4.5c shows identical polarization performance (after IR-correction) indicating a negligible effect of this layer on kinetic performance. Likewise, cyclic voltammograms performed under  $\text{H}_2/\text{N}_2$  (Figure 4.5d) also suggest no significant catalyst utilization drop (<5%) after the addition of the modified MPL layer to the CCL.

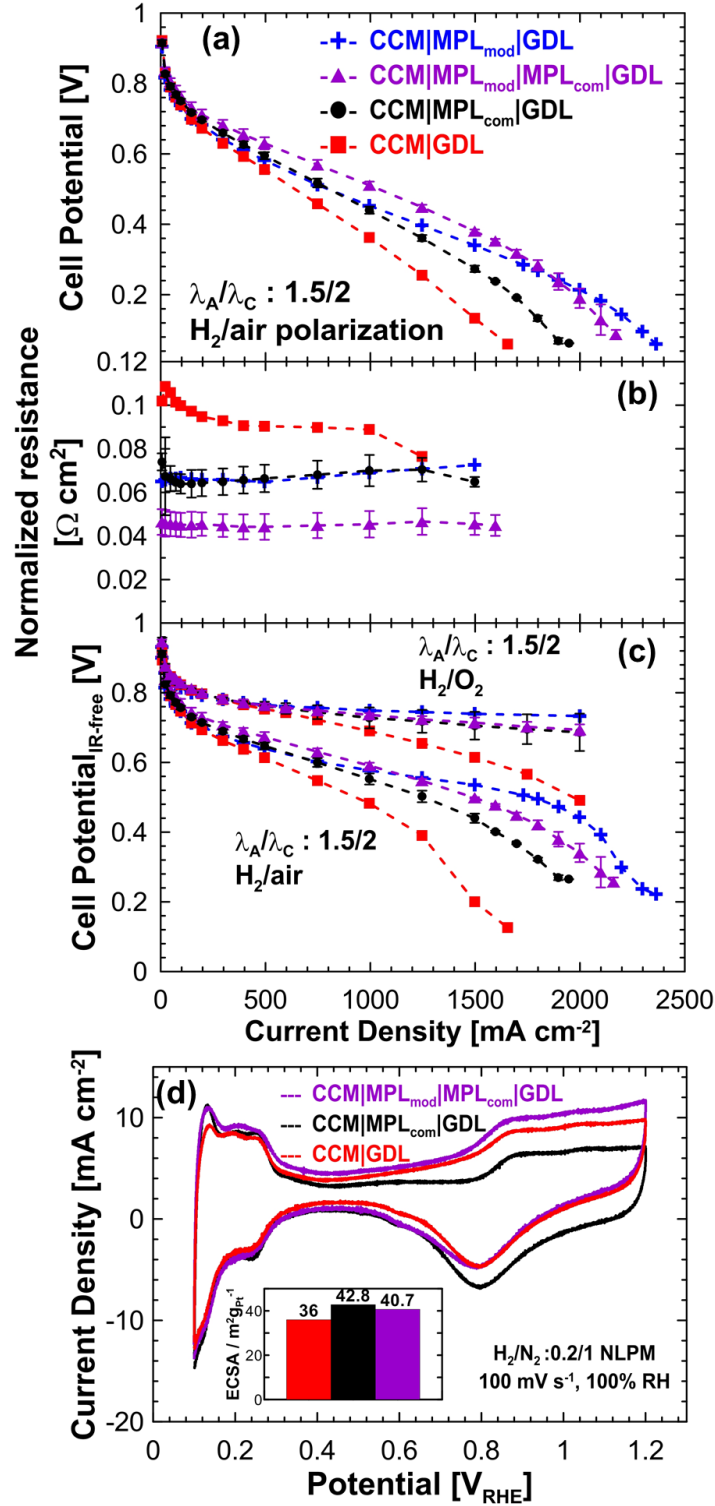


Figure 4.5: (a) Raw polarization curves, (b) high frequency resistance measured at 2.5 kHz, (c) IR-free polarization curves on H<sub>2</sub>/air and H<sub>2</sub>/O<sub>2</sub>, and (d) Electrochemically active surface area (ECSA) of MEAs with different architectures measured in fuel cell on H<sub>2</sub>/N<sub>2</sub>.

For a quantitative analysis of the enhancement effects (i.e., the cell resistance ( $R_{\text{ohmic}}$ ) and limiting current density ( $i_L$ )) observed in the modified MEA structure, a polarization overpotential correlation expressed by Equation (4.1) [166] was used to fit the polarization data obtained from the experimental work here and those of the literature [105]:

$$E = E^0 - (\ln i_0 + b \log j) - jR_{\text{ohmic}} - \left(\frac{RT}{nF}\right) \left(1 + \frac{1}{\alpha}\right) \ln \frac{i_L}{i_L - i} \quad (4.1)$$

where  $n = 2$ ,  $\alpha = 0.5$ ,  $F = 96485 \text{ C mol}^{-1}$ ,  $b = \text{Tafel slope (mA dec}^{-1}\text{)}$ ,  $T = \text{temperature (K)}$ ,  $E = \text{operational cell potential (V)}$ ,  $E^0 = \text{thermodynamic cell potential (V)}$ ,  $i = \text{current density (A cm}^{-2}\text{)}$ ,  $i_0 = \text{exchange current density (A cm}^{-2}\text{)}$ ,  $i_L = \text{limiting current density (A cm}^{-2}\text{)}$ , and  $R_{\text{ohmic}} = \text{ohmic resistance (}\Omega \text{ cm}^2\text{)}$ . In this fitting analysis, the kinetic parameters ( $j_0$  and  $b$ ) are set constant as indicated in Table 4.2 given the similar type of CCMs used here for all the experiments.

**Table 4.2. Fitted parameters of the baseline and the new architecture MEAs with a comparison to literature model**

|                                                      | Experiment                |                                       |                              | Model (ref [105]) |                    |
|------------------------------------------------------|---------------------------|---------------------------------------|------------------------------|-------------------|--------------------|
|                                                      | Baseline<br>(Figure 4.1b) | Modified<br>MPL only<br>(Figure 4.1c) | Double MPLs<br>(Figure 4.1d) | Baseline          | Perfect<br>contact |
| $R_{\text{ohmic}} / \text{m}\Omega \text{ cm}^2$     | 65                        | 65                                    | 45                           | 115               | 70                 |
| $i_L / \text{A cm}^{-2}$                             | 1.92                      | 2.28                                  | 2.12                         | 2.00              | 2.80               |
| $i_0 / \times 10^{-8} \text{ A cm}^{-2}_{\text{Pt}}$ | 4.2                       | 4.2                                   | 4.2                          | 3.8               | 3.8                |
| $b / \text{mV dec}^{-1}$                             | 103.6                     | 103.6                                 | 103.6                        | 81.8              | 81.8               |

The cell potential ( $E$ ) and current density ( $i$ ) values are then used to calculate the  $R_{\text{ohmic}}$  and  $i_L$ , for each set of polarization data. In the fitted resistance from the model [105], the perfect contact interface decreases the  $R_{\text{ohmic}}$  by 39% almost similar with the resistance value decrease obtained from the experimental data, i.e., 31% (Table 4.2). The reduction in interfacial resistance

with an MPL according to Swamy *et al.* can be attributed to better contact which facilitates electron transport from the MPL to the CL [109]. Based on their study, if the roughness of the MPL and CL surfaces is lowered by 50%, the interfacial contact resistance will be reduced by 40%. This suggests that by applying an MPL directly on the CCM we should improve the contact significantly (~50%). Similarly, the limiting current density shows an increase by 10% when the modified MPL is present along with the existing MPL and 19% when only the modified MPL is present, which is equivalent to 25% and 50% of the  $i_L$  increase, respectively, if the perfect contact occurs (Table 4.2). The potential difference plots of the experimental MEA with double MPLs and perfect contact simulation cases in Figure 4.6b show a similar trend and potential gain. The extent of performance improvements obtained in this new MEA architecture is significant for the overall performance of the PEM fuel cell especially for operation at high current densities.

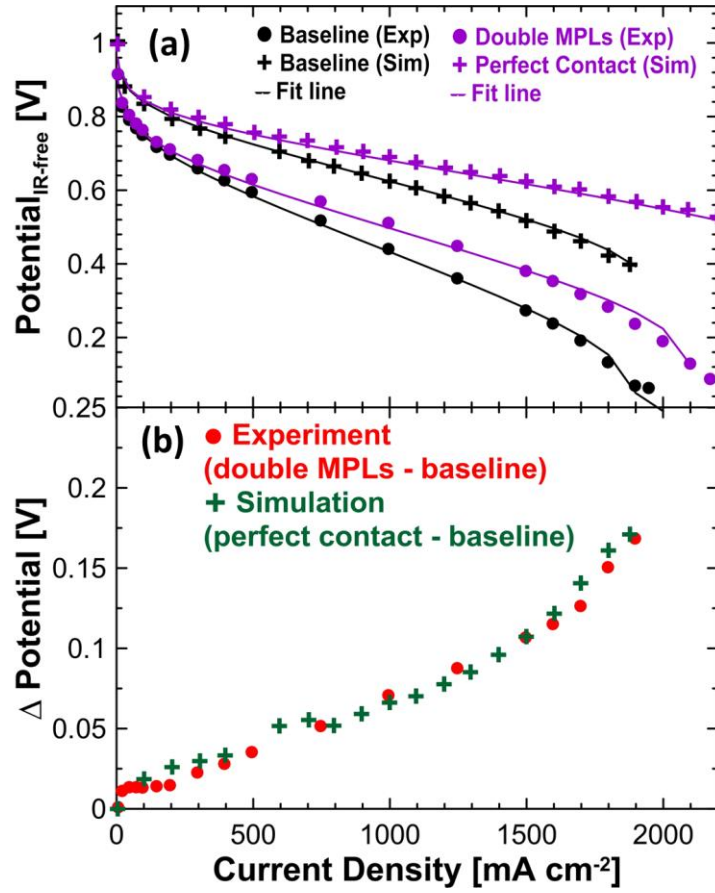


Figure 4.6: (a) Polarization curves with their fit lines, and (b) potential difference of baseline and modified MEAs for the computational model (from ref [105]) and experimental data.

## 4.5 Performance at High Humidity Conditions

### 4.5.1 Effect of Modified MPL Carbon Type on the Fuel Cell Performance

Three types of commonly used carbon black, namely Vulcan XC72R, Acetylene Black, and Black Pearls 2000, were used as the modified MPL materials in this study. In this modified MPL structure, the correlation between MPL morphology and performance are related in a similar fashion to that in the conventional MPL structure as discussed in Section 1.5.3.2.

#### 4.5.1.1 Performance in Kinetic Region

Components of the modified MPL (such as hydrophobic agent and solvent), which are directly deposited on the CCL, could conceivably cause detrimental impacts on the CL and lead to loss of kinetic activity of the catalysts. For instance, polyvinylidene fluoride as the hydrophobic agent and dimethylfuran (DMF) as solvent are shown to cause membrane shrinkage and, therefore, are not suitable for the modified MPL [167]. However, we have shown that VC-based MPL synthesized with a mixture of Teflon AF 1600 and FC-72 perfluoro-compound imposes no detrimental impacts on the catalytic performance of the ORR cathode [168]. Similarly, the BP- and AB-based MPLs prepared with similar components and synthesis routes in this study do not inflict any negative impacts on the kinetic performance of the CL. Figure 4.7 shows that all modified MPL materials tested here (at a modified MPL loading of  $0.8 \text{ mg}_{\text{carbon}} \text{ cm}^{-2}$ ) increase the kinetic performance with respect to that of the baseline which leads to improved  $\text{O}_2$  polarization curves. Therefore, the use of the modified MPL does not lead to any detrimental impacts on the catalyst layer. In contrast, an improvement in kinetic performance can be seen and is quite likely due to the improved contact between layers as also evidenced by lower electronic conductivity (Table 4.3). Among the modified MPL materials examined, BP shows the highest improvement in the kinetic performance followed by AB and VC carbon. The Tafel analysis of the  $\text{O}_2$  polarization data shows that  $i_0$  can increase as much as 29% from  $3.2 \times 10^{-8}$  to  $4.2 \times 10^{-8} \text{ A cm}^{-2}$  with the addition of the modified MPL on the catalyst layer (Figure 4.7b).

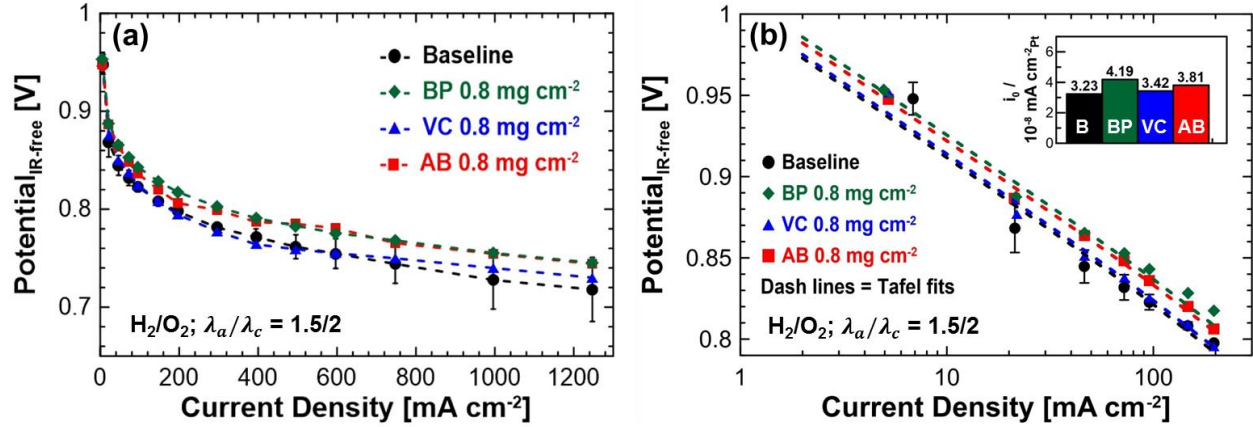


Figure 4.7: (a) Fuel cell polarization on H<sub>2</sub>/O<sub>2</sub> and (b) the Tafel plots up to 200 mA cm<sup>-2</sup> of the baseline and modified MPLs. Inset: exchange current density ( $i_0$ ) extracted from the H<sub>2</sub>/O<sub>2</sub> Tafel plots.

Table 4.3. Normalized HFR values of the baseline MEA and MEAs with a modified MPL tested in TP50 cell

| MPL      | MPL Loading (mg cm <sup>-2</sup> ) | HFR Value <sup>a</sup>       |                                         |
|----------|------------------------------------|------------------------------|-----------------------------------------|
|          |                                    | Average (Ω cm <sup>2</sup> ) | Standard Deviation (Ω cm <sup>2</sup> ) |
| Baseline | 0                                  | 66.3                         | 2.4                                     |
| VC       | 0.4                                | 56.5                         | 2.6                                     |
| VC       | 0.8                                | 45.1                         | 0.7                                     |
| VC       | 1.0                                | 65.6                         | 1.5                                     |
| VC       | 1.2                                | 76.8                         | 4.9                                     |
| AB       | 0.5                                | 41.1                         | 0.6                                     |
| AB       | 0.8                                | 56.0                         | 0.7                                     |
| AB       | 1.2                                | 50.2                         | 0.7                                     |
| BP       | 0.8                                | 55.9                         | 1.1                                     |

<sup>a</sup> the values reported are average values of the HFR measurements over ten different distinct points across the ohmic region of the respective polarization curve (i.e., 100 – 1500 mA cm<sup>-2</sup>)

#### 4.5.1.2 Performance in High Current Density Region

Figure 4.8 shows that in the H<sub>2</sub>/air fuel cells operating with 100% RH, MEAs with the modified MPL outperform the baseline MEA throughout the polarization curve. The reduced ohmic loss, caused by reduced resistance imposed by the modified MPL (Table 4.3), contributes to the improvement of overall performance particularly in medium to high current density

regions. With the level of carbon loadings tested, i.e.,  $0.8 \text{ mg}_{\text{carbon}} \text{ cm}^{-2}$ , the modified MPLs show a 15 - 32% reduction of the ohmic loss. Figure 4.8 shows that Acetylene Black-based modified MPL leads to highest gains across the polarization curve with clear and pronounced gains in the high current density regions. The higher gains observed with the AB-based modified MPL is most likely due to the more hydrophobic nature of AB carbon compared to those of VC and BP. A more hydrophobic layer retains less water in the vicinity of the catalyst layer thus inhibiting flooding of the CL and allowing more space for liquid water evaporation. The higher current density regimes ( $>1500 \text{ mA cm}^{-2}$ ), where more water is produced, are more sensitive to the presence of the modified MPL (Figure 4.8). AB-based modified MPL leads to a potential gain of 0.28 V, while VC- and BP-based MPLs yield gains of 0.11 and 0.13 V vs. baseline at  $1500 \text{ mA cm}^{-2}$ . It is also evident that MEAs with AB- and VC-based modified MPLs can still operate at a current density of  $2000 \text{ mA cm}^{-2}$  while the MEAs with no MPL and with BP-based MPL cannot reach these high current densities. This limitation is due to water accumulation which hinders air diffusion to the catalyst layer and, therefore, decreases the rate of the ORR.



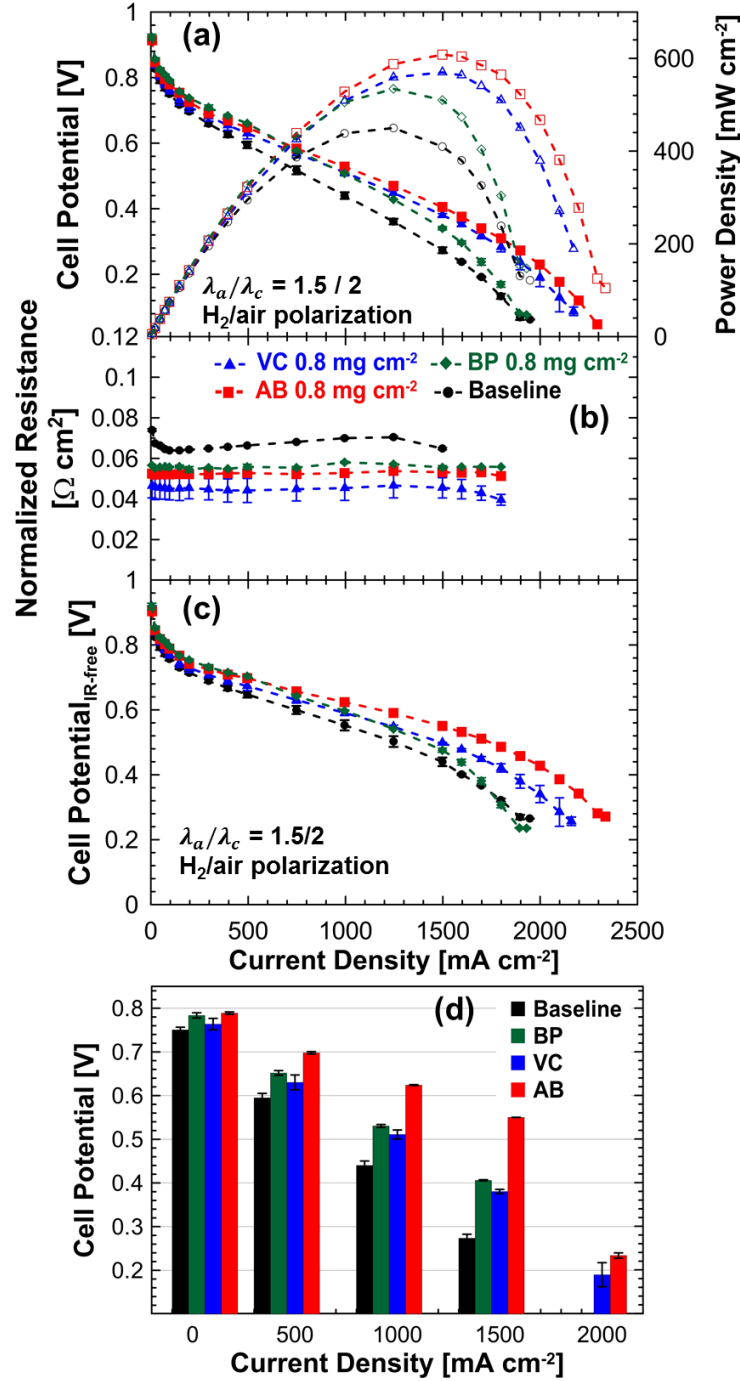
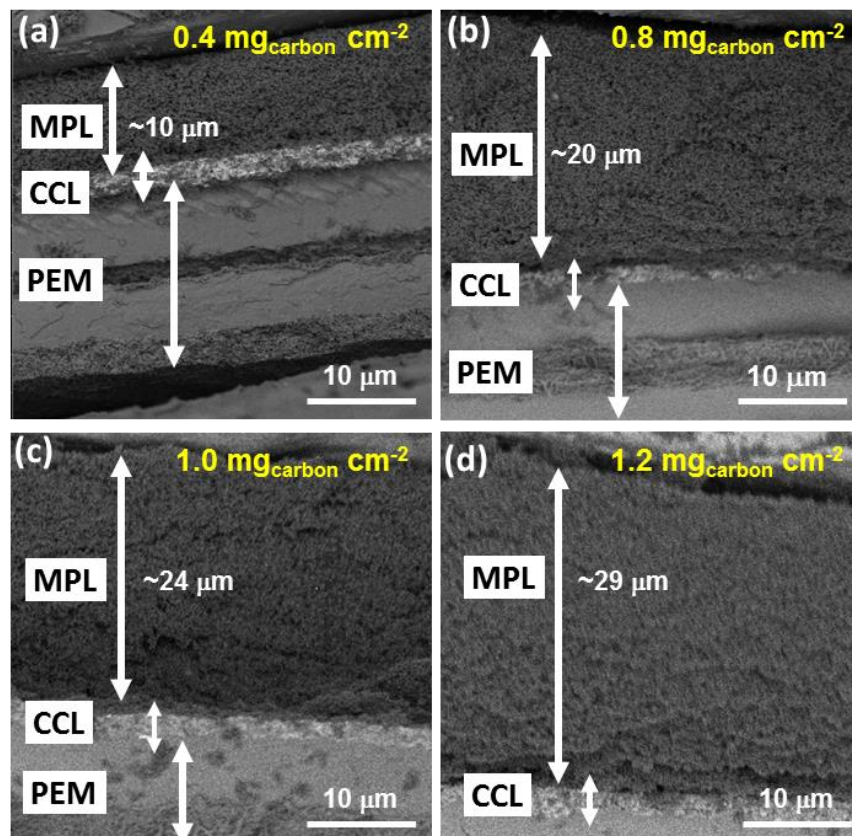


Figure 4.8: (a) Raw polarization and power density curves, (b) high frequency resistances measured at 2.5 kHz, (c) IR-free polarization curves, and (d) raw potential at specific current densities of MEAs with different types of carbon blacks tested with TP50 cell (on H<sub>2</sub>/air). (Note: measurements at 2000 mA cm<sup>-2</sup> were not possible for the baseline and BP samples because of excessive floodings).

This diminishing benefit of the BP-based MPL at high current density ( $>1500 \text{ mA cm}^{-2}$ ) can be attributed to the physical properties of BP. The surface area of VC, AB and BP show that BP has the largest surface area ( $1509 \text{ m}^2 \text{ g}^{-1}$ ) compared to VC ( $234 \text{ m}^2 \text{ g}^{-1}$ ) and AB ( $60 \text{ m}^2 \text{ g}^{-1}$ ), consistent with the observations reported elsewhere (Table 4.1) [80,169]. The less hydrophobic nature of BP as shown in Figure 4.3 is likely to cause more water absorption on its surface. Simon *et al.* study the effect of surface area by comparing AB-based MPL with different carbon surface areas ( $39 \text{ m}^2 \text{ g}^{-1}$  and  $\sim 68 \text{ m}^2 \text{ g}^{-1}$ ) and show that the lower surface area AB reduces the oxygen transport resistance with over-humidified conditions at  $50^\circ\text{C}$  [82]. Table 4.1 also shows that BP has the highest total pore volume, which is responsible for water pooling at high current densities. The higher hydrophilicity and the more porous nature of BP result in more significant mass transport-related losses. Zhang *et al.* have also demonstrated that conventional MPL consisting of BP has a lower limiting current density, i.e., maximum current density achieved, than the AB-based conventional MPL ( $900 \text{ mA cm}^{-2}$  vs.  $1300 \text{ mA cm}^{-2}$ ) at high humidity conditions [163].

#### 4.5.2 Effect of MPL Loading on Fuel Cell Performance

In general, the optimum thickness of the cathode MPL is a trade-off between the diffusion length of the permeating oxidant gas and the functionality of the layer. A thinner layer may benefit the performance as it provides a shorter gas diffusion path, but, a thicker MPL may improve the back-pressure effect, i.e. the removal of water in the CCL through the membrane, which enhances membrane humidification and reduces water saturation in the cathode side of the MEA [79].



**Figure 4.9: SEM Images (backscattered mode) of the CCM with different loadings of modified Vulcan XC-72R-based MPL: a) 0.4, b) 0.8, c) 1.0, and d) 1.2  $\text{mg}_{\text{carbon}} \text{cm}^{-2}$ . Thickness of MPL layer is proportional to the loading.**

For the conventional MPL structures commonly used, i.e., MPL coated on GDL, the optimum thickness is around 35 to 50  $\mu\text{m}$  for operations under high humidity (100% RH) [170]. The commercial SGC 29BC, for instance, has a 45  $\mu\text{m}$  thick MPL. Jordan *et al.* [79] show that for MPLs made of acetylene black, the highest performance gain with  $\text{O}_2$  is achieved at an MPL loading of 1.9  $\text{mg cm}^{-2}$ , which corresponds to the thickness of  $\sim 47 \mu\text{m}$ . Chen *et al.* [81], suggest that with AB-based MPLs the best performance, under high humidity of 100% RH, is achieved with AB loadings of about 1.5  $\text{mg cm}^{-2}$  corresponding to a thickness of around  $\sim 37.5 \mu\text{m}$ . For the modified MPL, deposited on the CCM, the optimum loading or thickness would arguably be

smaller than the conventional MPL structure deposited on the GDL because the commercial MPL still exists. The thickness of the modified MPL examined in this research thesis ranges from 0 to  $\sim 30 \mu\text{m}$ , which corresponds to mass loadings of  $0 - 1.2 \text{ mg cm}^{-2}$  (Figure 4.9). The MPL of the SGC29 BC GDL used in this study had a thickness of  $45 \mu\text{m}$ , thus the combined MPLs (conventional MPL on GDL and that of the CCM) studied here had a thickness range of 45 to  $75 \mu\text{m}$ . The thickness of the modified MPL increases proportionally with the MPL loading as shown in Figure 4.9.

#### 4.5.2.1 Masked TP50 Cell

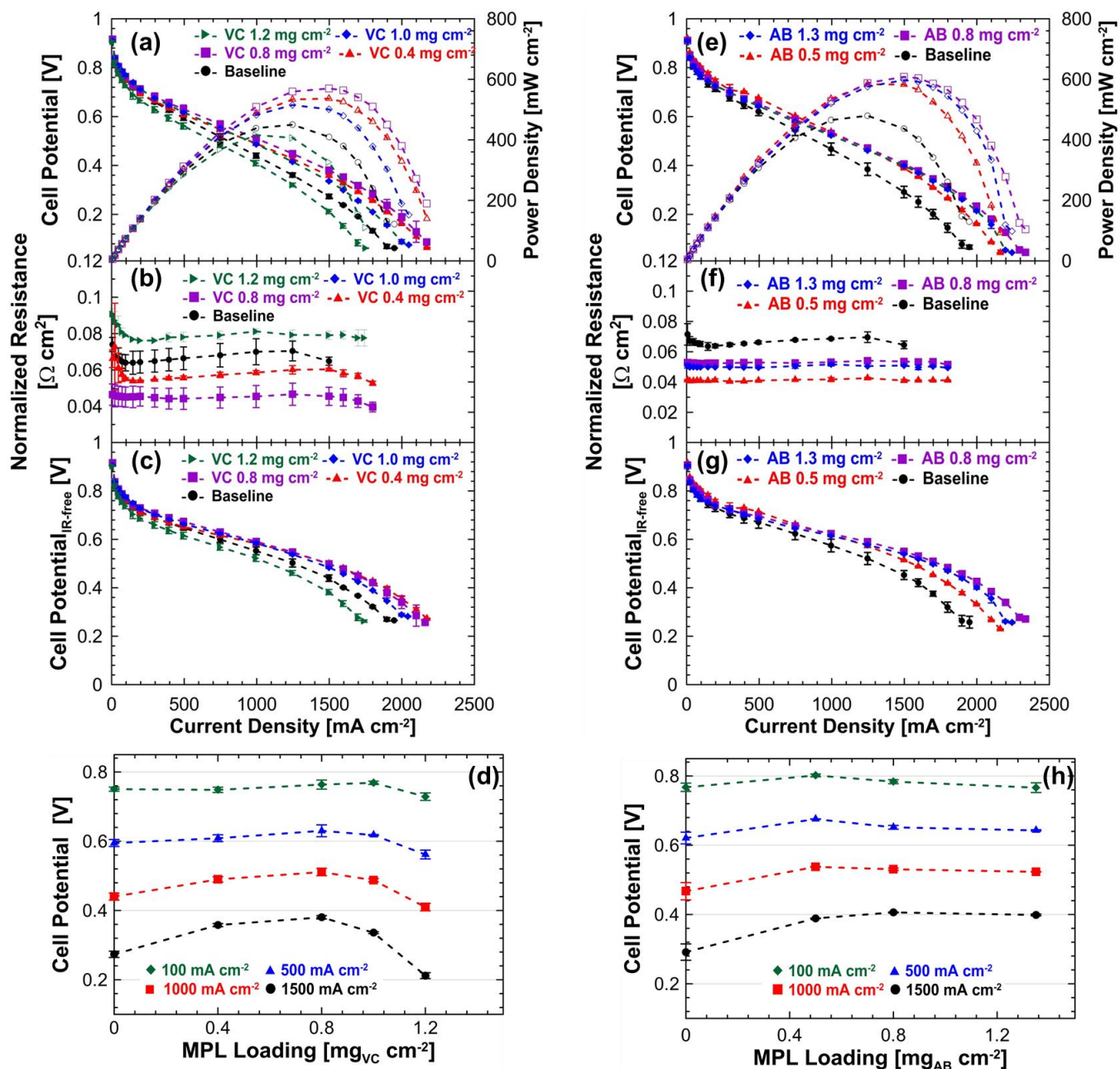
Figure 4.10 shows the performance of VC- and AB-based MPLs at various current densities with different carbon loadings at 100% RH. The error bars represent the standard deviations of multiple measurements and these included three different samples for the baseline MEA and one for each loading with two polarization cycles per sample. Figure 4.10d indicates that the fuel cell performance increases with addition of the VC-based modified MPL and reaches a maximum at a loading of  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$ . The maximum power density achieved at  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  is  $570 \text{ mW cm}^{-2}$  or 27% higher than that of the baseline with  $450 \text{ mW cm}^{-2}$  as shown in the polarization curves (Figure 4.10a-c) and summarized in Table 4.4. The potentials at high current densities ( $\geq 1000 \text{ mA cm}^{-2}$ ) also show a noticeable increase, for instance a 100 mV gain vs. baseline at  $1500 \text{ mA cm}^{-2}$ . The general trend, however, suggests that the performance with  $>0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  modified MPL decreases as the loading increases, and at  $1.2 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  the performance is lower than that of the baseline. The HFR measurements (Table 4.3) also show a similar trend where the HFR values decrease from the baseline sample to the sample with a VC of loading of  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  and decreases as the MPL layer thickness increases. The improved

performance is attributed to the better contact between layers and reduced gaps in the CCL|MPL interfacial region [101]. For the VC-based MPL, a very thick layer ( $>0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$ ) seems to lose these benefits presumably due to the presence of more void space in form of cracks and gaps which introduce discontinuity within the modified MPL. These void spaces reduce the layer electronic conductivity and tend to fill up with water, which leads to a decrease in performance at high currents [104]. The results clearly show that there is an optimum thickness for the modified MPL.

**Table 4.4. Maximum power density and power gain values of MEAs with a modified MPL vs. baseline extracted from polarization curves at 100% RH, 80°C**

| Carbon type        | Loading<br>( $\text{mg cm}^{-2}$ ) | Masked TP50, 150<br>kPag                           |                      | TP5, 100 kPag                                   |                      | TP5, 150 kPag                                      |                      |
|--------------------|------------------------------------|----------------------------------------------------|----------------------|-------------------------------------------------|----------------------|----------------------------------------------------|----------------------|
|                    |                                    | Max<br>power<br>density<br>( $\text{mW cm}^{-2}$ ) | Power<br>gain<br>(%) | Max power<br>density<br>( $\text{mW cm}^{-2}$ ) | Power<br>gain<br>(%) | Max<br>power<br>density<br>( $\text{mW cm}^{-2}$ ) | Power<br>gain<br>(%) |
| None<br>(Baseline) |                                    | 450.0                                              |                      | 490.8                                           |                      | 606.5                                              |                      |
| Black Pearl        | 0.8                                | 534.3                                              | 18.8%                |                                                 |                      |                                                    |                      |
| Acetylene<br>Black | 0.5                                | 583.4                                              | 29.7%                | 597.2                                           | 21.7%                | 671.2                                              | 10.7%                |
| Acetylene<br>Black | 0.8                                | 608.1                                              | 35.2%                | 671.0                                           | 36.7%                | 737.7                                              | 21.6%                |
| Acetylene<br>Black | 1.2                                |                                                    |                      | 568.0                                           | 15.7%                | 678.7                                              | 11.9%                |
| Acetylene<br>Black | 1.3                                | 597.3                                              | 32.7%                |                                                 |                      |                                                    |                      |
| Vulcan<br>XC72R    | 0.4                                | 536.2                                              | 19.2%                | 560.0                                           | 14.1%                | 666.4                                              | 9.9%                 |
| Vulcan<br>XC72R    | 0.8                                | 569.8                                              | 26.6%                | 515.0                                           | 4.9%                 | 629.2                                              | 3.7%                 |
| Vulcan<br>XC72R    | 1                                  | 515.0                                              | 14.5%                |                                                 |                      |                                                    |                      |
| Vulcan<br>XC72R    | 1.2                                | 415.8                                              | -7.6%                |                                                 |                      |                                                    |                      |

AB carbon also shows an increase in the performance for the loadings of 0 to 0.8 mg<sub>AB</sub> cm<sup>-2</sup>; however, unlike VC carbon, AB-based MPL imposes smaller loss of performance when the loading exceeds 0.8 mg<sub>AB</sub> cm<sup>-2</sup>. Figure 4.10h shows that at 1500 mA cm<sup>-2</sup>, AB-based modified MPL with a loading of 0.8 mg<sub>AB</sub> cm<sup>-2</sup> leads to a potential gain of 110 mV compared to the baseline. With this improvement, the 0.8 mg<sub>AB</sub> cm<sup>-2</sup> modified MPL shows highest power density of all the MPL carbon materials tested, i.e., 608 mW cm<sup>-2</sup> (158 mW cm<sup>-2</sup> or 36% higher than the baseline). Unlike the VC-based modified MPL, HFR values of the AB-based MPL do not increase as the loading exceeds 0.8 mg<sub>AB</sub> cm<sup>-2</sup> (Table 4.3). The relatively constant performance upon an increase in thickness with the AB-based MPLs up to a loading of 1.3 mg<sub>AB</sub> cm<sup>-2</sup> under high humidity conditions, and the further reduction in resistance indicate that adequate connectivity between the layers in the MPL is still maintained.



**Figure 4.10: Performance of MEAs with different loadings of VC-based MPL:** (a) Raw polarization and power density curves, (b) high frequency resistance measured at 2.5 kHz, (c) IR-free polarization curves, and (d) cell potential at various current densities; **Performance of MEAs with different loadings of AB-based MPL:** (e) Raw polarization and power density curves, (f) high frequency resistance measured at 2.5 kHz, (g) IR-free polarization curves, and (h) cell potential at various current densities

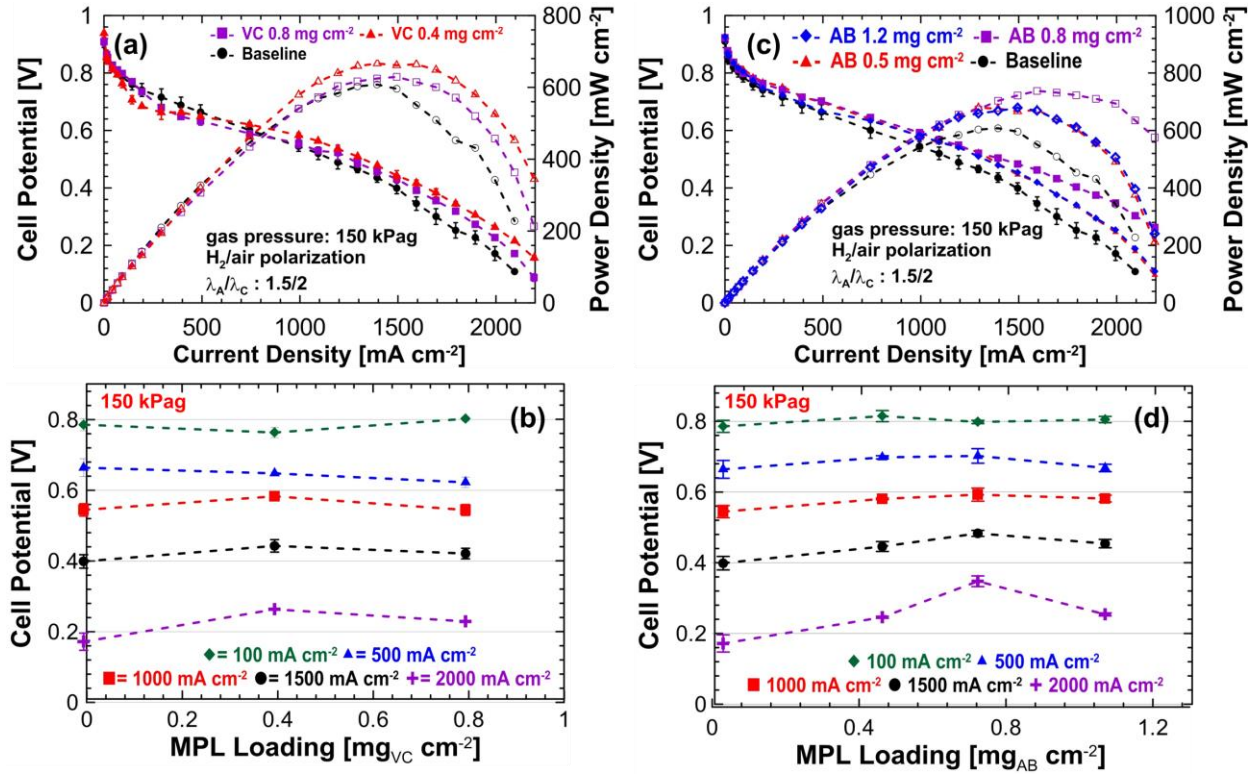
#### 4.5.2.2 TP5 Cell

To confirm the findings obtained with TP50 masked cell hardware, fuel cell tests with TP5 cell were performed for both AB and VC-based MPL with a similar loading range. Figure 4.11 shows the performance of the MEAs with additional VC-based modified MPL in TP5 cell. MEAs with 0.4 and 0.8 mg<sub>VC</sub> cm<sup>-2</sup> modified MPLs outperform the baseline, confirming the results from polarization with TP50 cell. At a current density of 1500 mA cm<sup>-2</sup>, the presence of a 0.4 mg<sub>VC</sub> cm<sup>-2</sup> and 0.8 mg<sub>VC</sub> cm<sup>-2</sup> MPL on CCM results in a gain of 50 and 30 mV potential vs. the baseline sample at gas pressures of 150 kPag, respectively. The maximum power density obtained in the presence of VC-based MPLs with a loading of 0.4 mg<sub>VC</sub> cm<sup>-2</sup> and 0.8 mg<sub>VC</sub> cm<sup>-2</sup> is ~666 mW cm<sup>-2</sup> or ~10% gain and ~629 mW cm<sup>-2</sup> or ~4% gain with respect to the baseline (Table 4.4). These results obtained with TP5 indicate the highest performance is reached with a loading to 0.4 mg<sub>VC</sub> cm<sup>-2</sup>. Considering both sets of experiments, for application of Vulcan Black based modified MPL, a higher performance gain is achieved at a lower MPL loading region, i.e., 0.4 to 0.8 mg<sub>VC</sub> cm<sup>-2</sup>.

The results of polarization tests of AB-based modified MPL with TP5 cell at 150 kPag show that the performance peaks at the loading of 0.8 mg<sub>AB</sub> cm<sup>-2</sup> (Figure 4.11c and d). The optimum loading obtained here is consistent with the one from TP50 cell. At higher current densities, for instance 1500 mA cm<sup>-2</sup>, MEA with 0.8 mg<sub>AB</sub> cm<sup>-2</sup> modified MPL shows a potential gain of 80 mV vs. baseline, which corresponds to a maximum power density of 737 mW cm<sup>-2</sup> or equivalent to ~22% higher than that of the baseline (Table 4.4). MEAs with 0.5 and 1.3 mg<sub>AB</sub> cm<sup>-2</sup> also show a higher performance from the baseline in the high current density region. MEAs with 0.5 and 1.3 mg<sub>AB</sub> cm<sup>-2</sup> increase the cell potential by 47 mV and 55 mV, which enable the cell to produce ~671 and ~678 mW cm<sup>-2</sup> (11 and 12% increase) of power density, respectively.



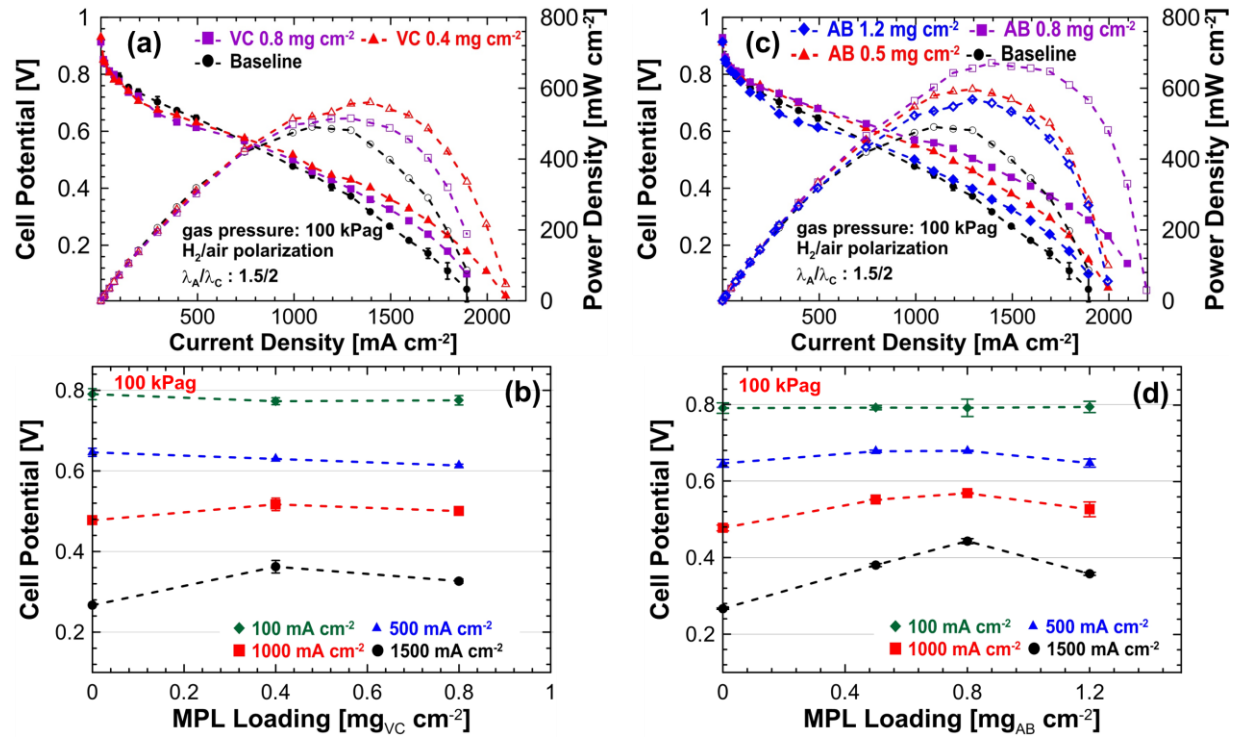
All three loadings tested were able to surpass the current density of 2000 mA cm<sup>-2</sup> with an air gas pressure of 150 kPag and outperform VC-based MPL with a similar loading.



**Figure 4.11: MEA polarization results with TP5 at 150 kPag gas back pressure: (a) Raw polarization and power density curves and (b) potential at various current densities of MEAs with different loadings of VC-based MPL; (c) Raw polarization and power density curves, and (d) potential at various current densities of MEAs with different loadings of AB-based MPL.**

Figure 4.12a and b show polarization plots of VC-based MPL with a lower gas pressure of 100 kPag tested with TP5 cell. The trend of the performance observed here is identical to that of a gas pressure of 150 kPag; however, a higher potential gain and percentage of power density gain is obtained. At a current density of 1500 mA cm<sup>-2</sup>, 100 mV and 60 mV potential gain is achieved by the application of 0.4 mg<sub>VC</sub> cm<sup>-2</sup> modified MPL and 0.8 mg<sub>VC</sub> cm<sup>-2</sup> (compared to 50 mV and 30 mV at 150 kPag air pressure). The maximum current density reached by the MEA with 0.4 mg<sub>VC</sub> cm<sup>-2</sup> modified MPL is 15% higher than the baseline, which is higher than 10%

percentage gain shown with 150 kPag gas pressure (Table 4.4). This doubled potential difference improvement and additional 50% improvement in maximum power density compared to the operation at 150 kPag gas pressure suggests that the impact of having the modified MPL is more critical at lower gas pressure operation, where mass transport losses are higher.



**Figure 4.12: MEA polarization results with TP5 at 100 kPag gas back pressure: (a) Raw polarization and power density curves and (b) potential at various current densities of MEAs with different loadings of AB-based MPL; (c) Raw polarization and power density curves and (d) potential at various current densities of MEAs with different loadings of VC-based MPL.**

Figure 4.12b and d, likewise, shows similar trend as the results with 150 kPag gas pressure operation. MEA with 0.8 mg<sub>AB</sub> cm<sup>-2</sup> modified MPL also shows the highest performance followed by 0.5 mg<sub>AB</sub> cm<sup>-2</sup> and 1.2 mg<sub>AB</sub> cm<sup>-2</sup>. Similar to the VC-based MPL, with a decreased gas pressure the potential difference between the baseline and modified MEAs also becomes wider. The best performing MEA with 0.8 mg<sub>AB</sub> cm<sup>-2</sup> modified MPL gains 176 mV voltage at a current density of 1500 mA cm<sup>-2</sup> at 100 kPag gas pressure, which also improves the maximum

power density by 37% (Table 4.4). These values are significantly higher than those obtained by a similar MEA under higher pressure of 150 kPag (i.e., 84 mV potential difference at 1500 mA cm<sup>-2</sup> and 21.6% maximum power density improvement). From these measurements, it is concluded that the optimum loading for AB-based modified MPL is achieved at 0.8 mg<sub>AB</sub> cm<sup>-2</sup> with the highest performance improvement leads to a ~37% gain in the cell maximum current density. For the VC-based MPL, a lower loading (0.4 to 0.8 mg<sub>VC</sub> cm<sup>-2</sup>) is preferable to achieve the most performance gain, and ~14% improvement in the cell maximum current density can be achieved with the optimum modified VC-based MPL applied.

#### 4.6 Performance at Low Humidity Conditions

One of the functions of the MPL is to force water with back diffusion from the cathode to the anode, leading to improved performance under dry conditions. During operations at dry conditions, the membrane requires extra humidification to maintain sufficient ionic conductivity otherwise cell potential decreases. To evaluate the impact of the modified MPL on the MEA performance, all MEAs were dried at 20% RH for 60 min at the cathode stoichiometry ( $\lambda_c$ ) of 8. Following the dry conditioning step, a polarization test was conducted at 20% RH. Drying leads to a lower performance of all MEAs compared to those of pre-drying. At 500 mA cm<sup>-2</sup>, the baseline MEA, for instance, reaches only 0.55 V at 20% RH (Figure 4.13) or 0.11 V lower than the cell potential at 100% RH.

Results of MEAs with AB-based MPL indicate a noticeable gain of performance and reduced resistance with loading  $\geq 0.8$  mg<sub>AB</sub> cm<sup>-2</sup>. Figure 4.13a shows that the cell potential of the MEA with 0.8 mg<sub>AB</sub> cm<sup>-2</sup> modified MPL is 0.47 V at 1000 mA cm<sup>-2</sup>, which is equivalent to 90 mV and 105 mV higher than that of the baseline MEA and the MEA with 0.5 mg<sub>AB</sub> cm<sup>-2</sup>

modified MPL, respectively. A thicker modified MPL (i.e.,  $1.2 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$ ) shows a lower performance than the  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$ , but still slightly outperforms the baseline MEA ( $\sim 36 \text{ mV}$  gain) and the MEA with  $0.5 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL ( $\sim 52 \text{ mV}$  gain). Reduction of normalized resistance (by 18% - from  $0.25$  to  $0.18 \Omega \text{ cm}^2$ ) and improvement of the exchange current density (by  $\sim 7\%$ ) confirm that the presence of AB at loadings  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  improves membrane hydration with respect to the baseline MEA (Figure 4.13d).

Figure 4.13d-f further show the effect of the VC-based MPL loading on the performance under low humidity. The cell potential gain with the presence of  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  *modified MPL* is noticeable while the gain after addition of the *modified MPL* with a loading of  $0.4 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  is almost negligible compared to the baseline. At  $1000 \text{ mA cm}^{-2}$ , for instance, a potential gain of  $0.4 \text{ V}$  is reached by adding  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  *modified MPL*, which is equivalent to  $\sim 40 \text{ mV}$  higher than the potential of both the baseline MEA and the MEA with  $0.4 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  *modified MPL*. The exchange current density and resistance values are calculated by fitting the raw polarization curve with the polarization overpotential correlation as described in our earlier publication [168]. The calculated and normalized resistance values shown in Figure 4.13f indicate a decreasing trend with an increase in loading, but a higher drop in resistance can be observed when loading increases from  $0.4$  to  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$ . The improved membrane hydration is also reflected by the improvement of the exchange current density.

Drop in the performance with a thicker layer can be attributed to a longer pathway for air to diffuse. On the other hand, as also reported elsewhere, a thicker MPL is beneficial to improve the back diffusion pressure [71]. The optimum performance, consequently, is a trade-off between a higher back pressure to the anode and shorter gas diffusion pathways. From the series of tests

conducted, it can be concluded that the optimum loading for this *modified* MPL structure at low humidity conditions is  $\sim 0.8 \text{ mg}_{\text{carbon}} \text{ cm}^{-2}$ .

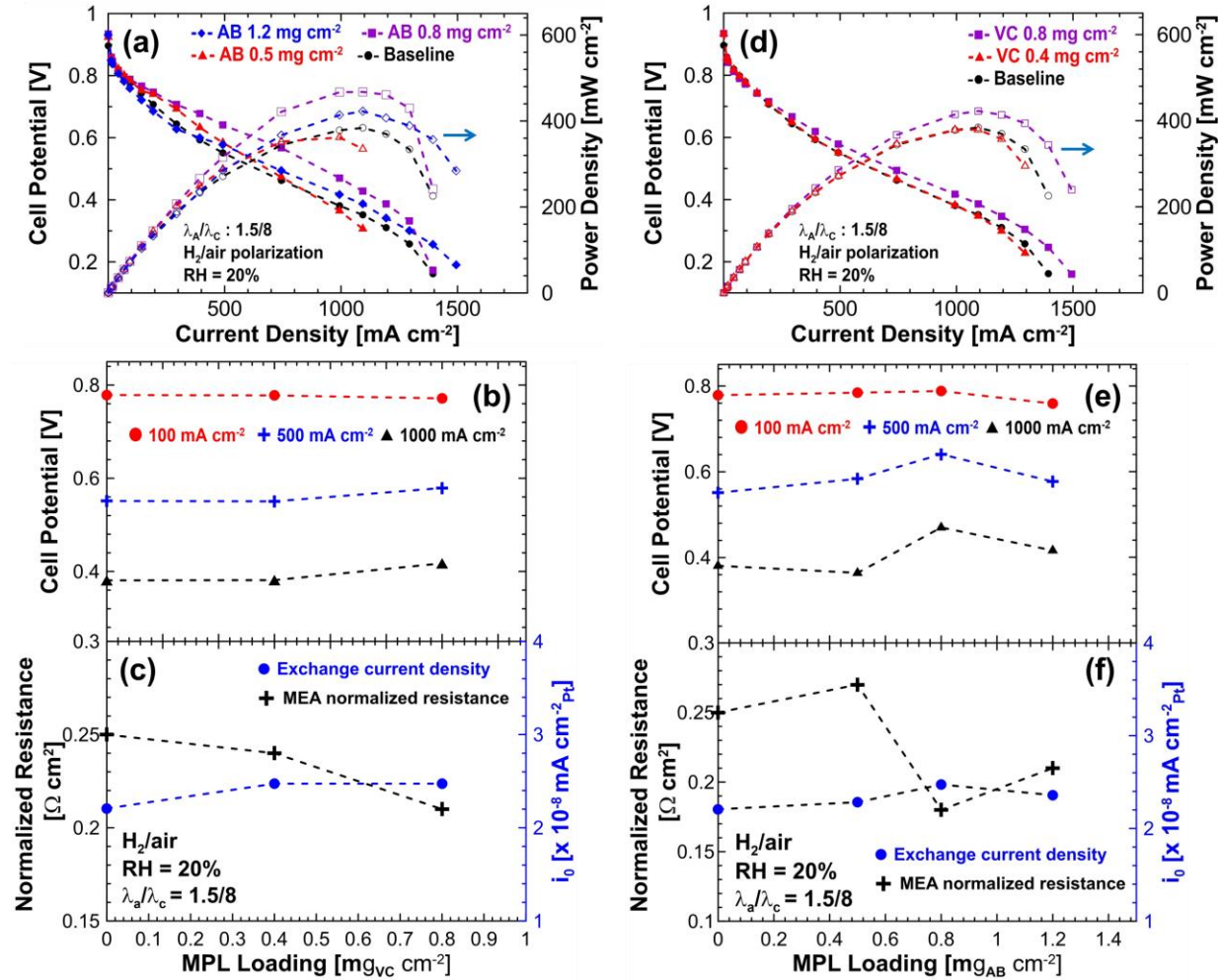
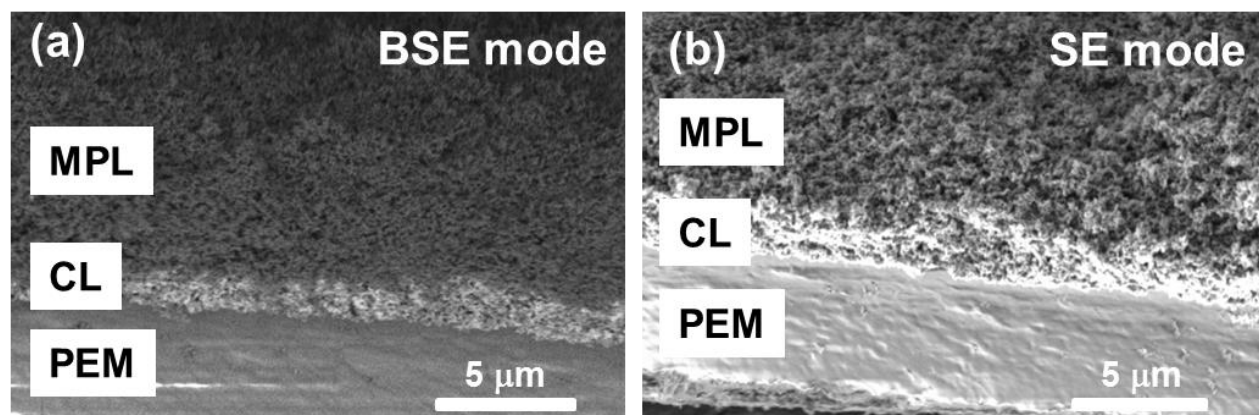


Figure 4.13: (a) VC-based MPL raw polarization and power density curves, (b) VC-based MPL cell potential at specific current densities, (c) VC-based MPL normalized resistance and exchange current density; (d) AB-based MPL raw polarization and power density curves, (e) AB-based MPL cell potential at specific current densities, (f) AB-based MPL normalized resistance and exchange current density obtained from polarization measurements performed at 20% RH with a TP5 cell hardware and a gas pressure of 150 kPag.

#### 4.7 Longer Term Performance

Physical durability of this modified MPL architecture was examined using a prolonged flowing hot water test inside the fuel cell hardware under normal operational cell pressure. The

hot water was flowed into the cathode side of the MEA. After 40 hours of exposure with 80°C hot water, the modified MPL appears to remain intact (adhered to the catalyst layer) as shown in Figure 4.14. This clearly shows that the structure maintains excellent stability even after an unusually harsh test like longer term hot liquid water exposure.



**Figure 4.14: SEM images with (a) BSE and (b) SE mode of modified MPL remains adhered to CCM after 40 h of hot water exposure**

Figure 4.15a shows the results of the long-term performance tests of the baseline MEA and the best performing MEA from the polarization tests under 100% RH, i.e, MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL. Under a prolonged test at 100% RH performed for 50 h, the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL obtains a high potential at the beginning of the test but declines sharply during the first 12 hours. This unsteady behavior is likely due to the fresh MEA still in conditioning phase while the MEA has not equilibrated yet. After the initial 12 h period, the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL shows a steady performance drop with a rate of  $\sim 2.6$  mV per hour. The baseline MEA, on the other hand, shows a steadier behavior for the entire 50 h test, but with a higher drop than the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL. The baseline MEA loses are  $\sim 4.1$  mV per hour at constant current density hold of  $1000 \text{ mA cm}^{-2}$ . The lower degradation slope exhibited by the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL suggests that it can

handle the excess water produced in the MEA better than the baseline due to the presence of the modified MPL even after a ~50 h operation at high current densities confirming the findings shown with polarization measurements. Using SEM analysis we reported that the modified MPL remains intact even after ~40 h operation under fuel cell testing conditions [168]. At the end of 50 h test, the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL still outperforms the baseline by 100 mV at  $1 \text{ A cm}^{-2}$ .

Figure 4.15b compares the performance of the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL and the baseline MEA under a prolonged dry test (~20% RH) for 25 hours. In general, the cell potential for the two different MEAs show a significant difference throughout the duration of the test compared to the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL and show an increase of about >0.08V. The performance of the baseline indicates a constant performance loss due to drying as manifested by a consistent negative slope across the curve. The MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL, on the other hand, shows a more stable profile despite sharper initial (<5 h) drops. During the 25 h period testing period, the baseline MEA's performance is affected more by the drier gas feed as evident by the more pronounced performance drops. The performance of the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL under a prolonged dry test overall show a less performance loss than the baseline. The baseline MEA drops from 0.48 V to 0.3 V (~38% loss) with a degradation rate of ~4.4 mV per hour while the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL drops from 0.6 V to 0.44 V (~26% loss) with a degradation rate of ~2.1 mV per hour. The lower performance slope of the MEA with  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  modified MPL suggests the ability of the MEA with modified MPL to prevent the hydration not only for a shorter term, but also for a long-term performance. The presence of a  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  AB-based modified MPL, therefore, benefits both short- and long-term performances under both wet and dry conditions.



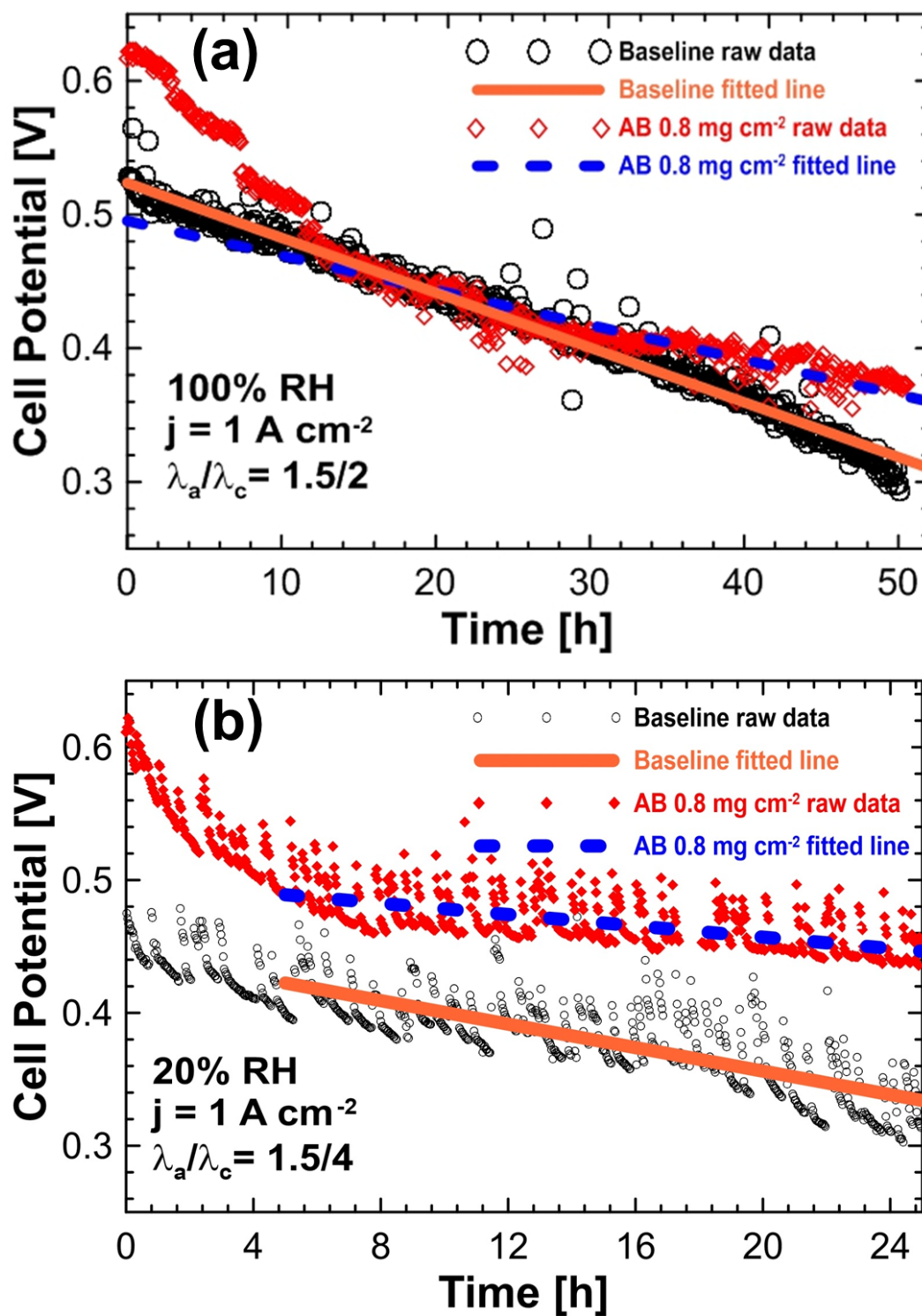


Figure 4.15: Long-term performance of the baseline vs. AB 0.8 at 1000 mA cm<sup>-2</sup> performed at (a) 100% RH for 50 h and (b) 20% RH for 25 h.



## 4.8 Conclusions

A new method to synthesize and to apply a hydrophobic PTFE-mixed modified MPL on a thin cathode catalyst layer ( $\sim 3 \mu\text{m}$ ) was successfully demonstrated in this research thesis. A new MEA architecture with a modified microporous layer (MPL) consisted of  $0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  deposited directly on the CCM physically shows reduced gaps at the cathode catalyst layer and the adjacent MPL interface. These gaps can potentially be filled with water at high current density operations and cause noticeable fuel cell performance drop. Polarization tests under wet conditions reveal that this new architecture with Vulcan Carbon-based MPL can reduce the estimated cell contact resistance by 31% and increase the limiting current density by about 10% vs. the current CCM-based MEA structure by reducing these gaps. The increase in limiting current density not only enables the fuel cell to produce higher power density but also lowers the capital cost as the size of the stack will be reduced. With this new modified MPL structure, CCM manufacturers can also add more values to their existing CCM products as well as improve the flexibility of the CCM products for a wider range of applications.

Application of acetylene black (AB) with any loading between  $0 - 1.3 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  and Vulcan XC72 (VC) with any loading between  $0 - 1.0 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  as the modified MPL with 20% PTFE shows improvement in fuel cell performance, particularly in the higher current density region. Modified MPL consisted of Black Pearl 200 (BP) carbon black at a loading of  $0.8 \text{ mg}_{\text{BP}} \text{ cm}^{-2}$ , on the other hand, imposed the highest performance improvement in the kinetic region. The loading of  $0.8 \text{ mg cm}^{-2}$  or equivalent to  $20 \mu\text{m}$  thick is found to be the optimum loading for AB-based modified MPL, while the modified MPL with loading of  $0.4 - 0.8 \text{ mg}_{\text{VC}} \text{ cm}^{-2}$  (i.e.,  $10 - 20 \mu\text{m}$  thick) shows the highest improvement with VC-based modified MPL. The application of modified AB-based MPL can achieve a maximum power gain of  $\sim 37\%$  compared to the

baseline, while the highest maximum power density gain demonstrated by VC-based modified MPL is  $\sim 27\%$  at 100% RH. These significant gains are beneficial especially for the operation of MEAs with thinner catalyst layer under wet conditions. It is suggested that the addition of  $0.8 - 1.3 \text{ mg cm}^{-2}$  of modified MPL to the CCL results in an enhanced performance under dry conditions, which was attributed to improved hydration due to higher back diffusion of water. Having a thicker modified MPL ( $>0.8 \text{ mg cm}^{-2}$ ), however, generally imposes more detrimental effect on performance, presumably due to a higher temperature in the CCM, which causes more evaporation and dryer membrane. Prolonged performance tests under high and low humidification also reveal that the presence of the AB-based MPL with a loading of  $0.8 \text{ mg}_{\text{AB}} \text{ cm}^{-2}$  still outperforms the baseline after 50 h under high humidification and after 25 h under low humidification. A more stable performance is demonstrated by the MEA with a modified MPL was indicated by a lower performance decline with long term tests under wet and dry conditions. The modified MPL structure also remained intact physically after 40 h of exposure to water at the fuel cell temperature.

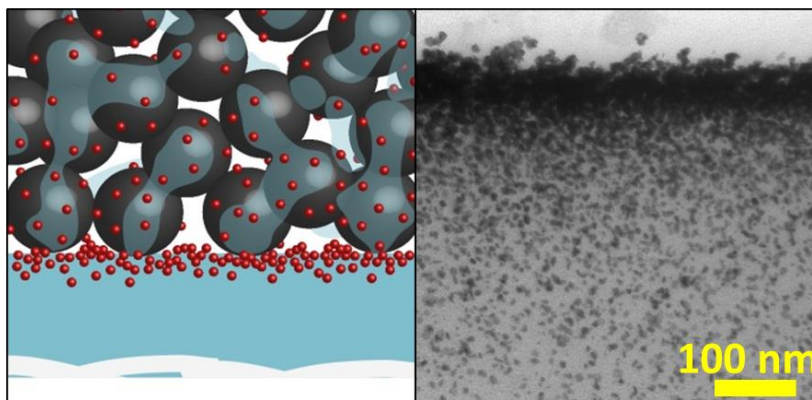
## Chapter 5: Conclusions

### 5.1 Conclusions

This thesis examines the impact of the interface modifications on the operational flexibility of the PEM fuel cell, which is considered as one of the most critical parameters for automotive applications. With improved operational flexibility, a fuel cell can maintain its performance under wide ranges of humidity, current density, duration, etc. The future benchmark of using a lower Pt loading catalyst ( $\sim 0.125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  electrode) is a major challenge to be considered as a thinner catalyst layer results in a lower performance due to excessive flooding in the CL. In this thesis, two approaches to the modification of the CL interfaces were used to improve the overall performance, with a strong emphasis on the operational flexibility of the fuel cell. The two approaches are i) modification of the PEM|CL interface with an electroless Pt layer in the membrane subsurface, and ii) modification of CL|MPL interface with modified MPL applied on the catalyst layer.

#### Modification of the PEM|CL interface:

- Electroless Pt layer in the membrane subsurface with a low Pt loading ( $< 100 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ) has been synthesized with the modified non-equilibrium electroless Pt synthesis method at a  $30^\circ\text{C}$  reaction temperature (Figure 5.1).
- Pt loading can be controlled by changing the reduction time and increases almost linearly with the reduction time at  $30^\circ\text{C}$  up to a maximum loading of  $\sim 70 \text{ } \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . At the near-saturated loading ( $\sim 12 - 16.5 \text{ min}$  reduction time), the plateau region is observed as a longer reduction time seems to have little to no effect on loading.



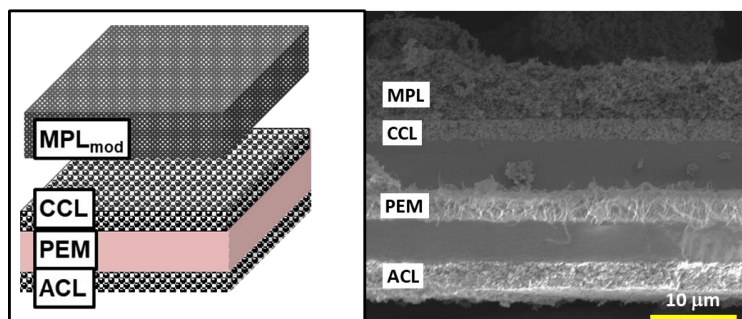
**Figure 5.1: Schematic and TEM image of the electroless Pt structure in the membrane subsurface**

- Simple geometric-based models derived from XRD and ECSA can be used to predict the growth mechanism of Pt in the layer (assuming a spherical shape of the Pt particle). In the loading range studied an increase in loading results in Pt particle growth and improved interparticle connectivity.
- The Pt utilization, which is an indicator of the degree of connectivity of these Pt sublayer particles (100% utilization means all particles are connected and contribute to the measured ECSA), increases with loading. The increase in Pt utilization can be determined in terms of the grain size, i.e.,  $\propto r_{\text{Pt-grain}}^{1.80}$  with the highest Pt utilization obtained in the range studied  $\sim 22\%$  (at  $78 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ )
- The reduction of the hydrogen crossover current is proportional to the loading of the electroless Pt layer. The presence of a  $78 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  electroless Pt layer shows up to 65% reduction of the  $\text{H}_2$  crossover current.
- The exchange current density and the proton concentration involved in the ORR decreases as the electroless Pt loading increases. Similarly, the proton conductivity ( $\sigma$ ) of the electrolessly deposited Pt membrane appears to be inversely proportional to the loading of the Pt layer embedded in its subsurface.

- The performances of the GDE-based MEAs with the electroless Pt layer tested with a 1D parallel cell demonstrate a clear benefit of the electroless Pt with loadings  $<20 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ . MEAs with such a low electroless Pt loading have a comparable performance to the baseline and yet improved the performance at low humidity conditions due to a better humidification of the membrane and the ionomer in the catalyst layer.
- In a test with an 18 h continuous humidity cycling operation, the electroless Pt layer with a low loading of  $17 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  shows a higher potential and a lower resistance in the dry period and equivalent performance in the wet periods.

#### Modification of CL|MPL interface:

- A new MEA architecture with a hydrophobic, PTFE-based modified microporous layer (MPL) deposited directly on the CCM physically was successfully fabricated and showed reduced gaps between the cathode catalyst layer and the adjacent MPL interface (Figure 5.2).



**Figure 5.2: Schematic and the SEM image of the modified MPL deposited on the CCM**

- The application of Teflon AF 1600, a perfluorocompound, has enabled sintering of PTFE with the CCM at a lower temperature ( $165^{\circ}\text{C}$ ), which is harmless to the membrane.

- Polarization tests under wet conditions reveal that this new architecture with Vulcan Carbon-based MPL can reduce the estimated cell contact resistance by 31% and increase the limiting current density by about 10% vs. the current CCM-based MEA structure by reducing these gaps.
- Application of acetylene black (AB) with any loading between 0 – 1.3 mg<sub>AB</sub> cm<sup>-2</sup> and Vulcan XC72 (VC) with any loading between 0 – 1.0 mg<sub>VC</sub> cm<sup>-2</sup> as the modified MPL with 20% PTFE shows improvement in fuel cell performance, particularly in the higher current density region.
- Application of Black Pearl-based modified MPL with a loading of 0.8 mg<sub>BP</sub> cm<sup>-2</sup> results in the highest gain in the fuel cell ORR catalytic performance.
- The optimum loading for the AB-based MPL is 0.8 mg<sub>AB</sub> cm<sup>-2</sup> (equivalent to ~20 mm thick MPL), while for the VC-based MPL is ~0.4 - 0.8 mg<sub>VC</sub> cm<sup>-2</sup> (equivalent to ~10-20 mm thick MPL). With these best performing loading, the maximum power density can be improved by ~37% and ~27% with AB and VC based MPLs, respectively.
- The addition of 0.8 – 1.3 mg cm<sup>-2</sup> of modified MPL to the CCL results in an enhanced performance under dry conditions due to improved hydration as a result of higher back diffusion of water. Having a thicker modified MPL (>0.8 mg cm<sup>-2</sup>), however, generally lower the performance compared to the performance at 0.8 mg cm<sup>-2</sup> because of the longer diffusion pathway of air in the MPL
- Prolonged performance tests under high and low humidification also reveal that the presence of the AB-based MPL with a loading of 0.8 mg<sub>AB</sub> cm<sup>-2</sup> still outperforms the baseline after 50 h under high humidification, and after 25 h under low humidification with a lower performance drop vs. time.

## 5.2 Future Recommendations

### Half-cell Development:

- For the half CCM samples, the introduction of a membrane in the sample acts as a barrier for water removal from the catalyst layer to the electrolyte. The product water from the ORR will then be accumulated in the catalyst layer porous structure and causes a performance drop. Improvement in the cell design would involve creating a water removal port from the back or the side of the cell to prevent water accumulation.
- At high current density, bubbles are formed rapidly on the counter electrode and affect the measurement or reduce the electrode surface contact area with electrolyte. Reduction of contact between bubbles generated at the counter electrode and the working electrode, e.g., with a stirrer, and the use of a larger counter electrode would be useful for the improvement of half-cell measurement.

### Modification of the PEM|CL interface:

- The stability of the borohydride can be improved by increasing the pH of the  $K_2SO_4$  solution on the other side of the deposition cell. A more stable borohydride as a reducing agent will result in a higher concentration and a thicker Pt layer deposited. A thicker and lower density of the Pt sublayer might be more suitable for gas crossover reduction purpose, i.e., improving membrane chemical durability.

- For an MEA assembled with the GDE method, the presence of the low loading electroless Pt sublayer can also potentially improve the ECSA of the cathode catalyst layer (CCL) attached to it because of the better connectivity between the membrane and the CCL. The opposite (i.e., the improvement of the ECSA of the electroless layer due to the contact with cathode catalyst layer) may also be true. However, at higher electroless Pt loading, the impeded proton may reduce the ECSA and diminish the gain. A more systematic study needs to be done to determine the optimum loading to achieve the highest ECSA.
- A longer durability test following the DOE recommendations (20,000 cycles of relative humidity cycling at OCV) would be useful to determine the improvement in chemical and mechanical stability of the fuel cell as a result of lower hydrogen crossover and improved hydration imposed by this electroless Pt layer.
- This structure can be further modified by adding a thin layer of carbon at the membrane subsurface before deposition of an electroless Pt layer. The initial attempt of this work is presented in Appendix B.6. This thin carbon layer (<100 nm thick) can be applied by spraying a low concentration carbon black solution to the membrane or using high vacuum sputtering with a carbon rod. This structure would be expected to improve the Pt utilization and enhance functionality of this electroless Pt layer.
- Investigate any mechanical modifications of the PEM to improve the density of the deposited electroless Pt layer while retaining hydrophilic channels for water transport.

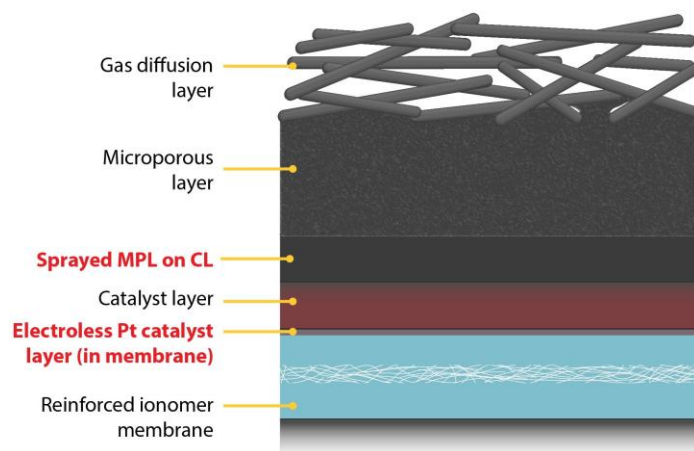


#### Modification of CL|MPL interface:

- Other carbon types, particularly nanoengineered structures with a high fraction of microporous pores and high hydrophobicity would also be a good candidate for this new modified MPL architecture for further improvement of the performance. The hydrophobicity of this layer could also be improved by applying a higher composition of PTFE (>20%). A composite carbon (for instance: BP and AB) which combines the merits of two or more carbon types could also be considered as an improved MPL material.
- A more thorough study to investigate the effect of having only the modified MPL (Figure 4.1d) with different synthesis parameters (thickness, carbon type, PTFE fraction) would be useful to determine the limit of this layer, in particular for the durability of the MEA. As this modified MPL is typically thinner than the existing MPL, it might not as efficient as the existing MPL in acting as a barrier from the carbon fiber penetration from the GDL.
- Study the impact of the modified MPL on the long term stability test of the MEA using the DOE protocol.

#### Combination of both modifications:

- Test an MEA with both modifications, i.e., electroless layer Pt and modified MPL deposited on the catalyst layer, in place (Figure 5.3) under different testing conditions.



**Figure 5.3: Schematic of an MEA architecture with both electroless Pt and modified MPL modifications**

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## **Appendices**



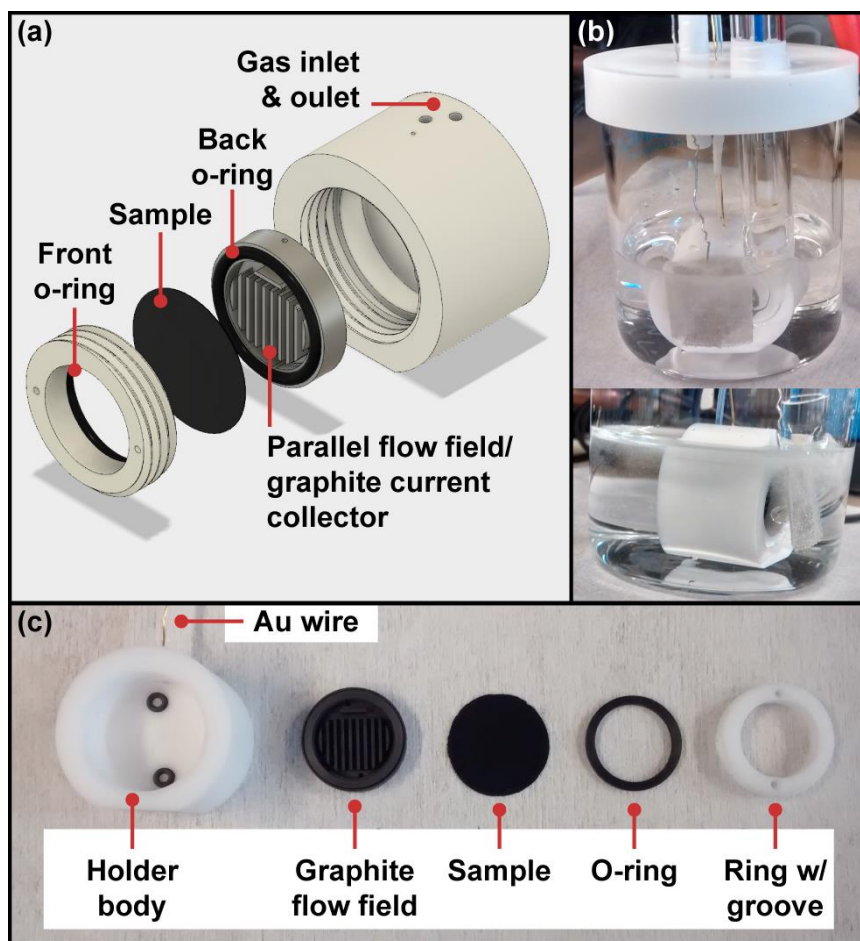
## Appendix A - Supporting Information for Experimental Design

Appendix A includes all hardware designs, components, drawings, and dimensions; method to assembly a masked MEA, and process flow diagram for water diffusion experiment.

### A.1 Half-cell Design

Materials with high chemical resistivity such as glass and polytetrafluoroethylene (PTFE) were selected for the cell used. The PTFE sample holder components were designed and manufactured in-house. Large Viton o-rings (Dash 016, McMaster-Carr) were selected for sealing on both the front and back faces of the sample due to their excellent chemical resistance but higher compressibility than PTFE-coated o-rings. A square profile o-ring causes less sample damage on disassembly/reassembly, yields a well-defined exposed surface area, and provides better sealing compared to a conventional round-profile o-ring. Small Viton o-rings (Dash 001.5, McMaster Carr) were used to seal around the gas inlet and outlet between the PTFE main body and the graphite flow field. PTFE tubing (1/32" ID, 1/16" OD, semi-clear white, McMaster-Carr) was press fit in the gas inlet and outlets of the main body. Tubing can be omitted on the gas outlet side to reduce the pressure drop and facilitate expulsion of product water. A graphite flow field with a modified parallel channel geometry was machined from graphite (surface resistivity =  $2.2 \times 10^{-3}$  ohms/sq., 9121K67, McMaster Carr). The graphite flow field also acts as the current collector and includes an o-ring groove for sealing on the back side of the sample. Electrical contact to the graphite current collector was made at the top with an Au wire (0.5 mm diameter, 99.95%, Alfa Aesar) which was threaded through a hole in the sample holder body. A large Pt gauze (52 mesh, 99.9%, Alfa Aesar) and Pt wire (0.5 mm diameter, 99.95%, Alfa Aesar) were used to fabricate a high-surface area flag counter electrode. Flat-rimmed glass beakers and

custom-designed Luggin capillaries were sourced externally (Cansci Glass Products Ltd). A glass frit (Ace dispersion tube, porosity D, Sigma-Aldrich) was used to purge the cell headspace with either Ar or O<sub>2</sub>. Ar (99.999%, UHP, Praxair) and O<sub>2</sub> (99.993%, UHP, Praxair) were used as received and the gas flow rate to the sample holder was controlled via a flowmeter (150 mm, Key Instruments). Gas purging of the cell headspace was controlled separately (> 1500 SCCM). All gases were delivered at a pressure of 1 atm. A custom PTFE cap with holes for all electrodes and leads was fitted over the glass beaker to facilitate assembly.



**Figure A.1:** Schematic of half-cell sample holder including graphite flow field, (b) photo of assembled sample holder in electrochemical cell, and (c) photo of individual half-cell components in assembly order.

## A.2 Glassware Handling

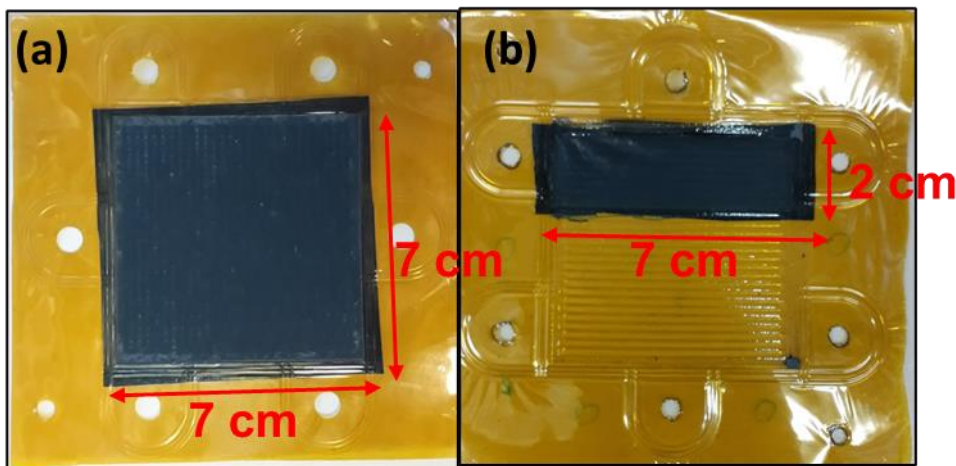
The cell cleaning procedure and the choice of acid supplier are paramount to reducing contamination for fuel cell catalyst studies. In this work, glassware cleaning was applied regularly for the half-cell and floating cell apparatus. Deionized (DI) water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ,  $< 5$  ppb TOC water, Milli-Q Integral 5, Fisher Scientific) was utilized for component cleaning and acid dilutions. The protocol used for cleaning and preparation is described as following:

- i) Components were scrubbed with soap (e.g., Sparkleen) and DI water then rinsed thoroughly;
- ii) Components then were soaked overnight in concentrated sulfuric acid (95-98%, Certified ACS Plus, Fisher Scientific) then rinsed thoroughly;
- iii) Components were boiled five times in DI water, with a new batch of water used for each cycle; and
- iv) Components were rinsed a final time and allowed to air dry or dried using lint-free paper.

## A.3 Masking the MEA

Masking the MEA is a method to reduce the active area of a CCM due to material constraints. In this work, the masking MEA method is applied to mask a  $49 \text{ cm}^2$  ( $7 \text{ cm} \times 7 \text{ cm}$ ) MEA into a  $14 \text{ cm}^2$  ( $7 \text{ cm} \times 2 \text{ cm}$ ) MEA as shown in Figure A.2. Figure A.3 shows that the full size MEA and the masked MEA perform similarly up to  $1000 \text{ mA cm}^{-2}$ . This repeatable performance indicates that the masking method has negligible impact on the performance at low current densities. At higher current densities, on the other hand, the masked MEA has more mass transport losses. With the masked MEA, the flow rate of the gas is lower than the normal flow

rate, while the pathway of flooded channel remains the same leading to higher mass transport diffusion resistance. This explanation is also supported by the test at a higher cathode stoichiometry (i.e., higher flow rate) which shows a closer polarization performance gap between the masked MEA and the full size MEA. Polarization curves of both the masked MEA and the full size MEA conducted on  $O_2$ , where the concentration of reactant is significantly higher, show very identical performance. The absence of mass transport limitations on the oxygen polarization eliminates the performance difference shown by the two types of MEAs. It can therefore be concluded that the masking method has a negligible impact on the kinetic performance and but imposes a greater mass transport resistance. A more flooded cell resulting from the masking method is useful in this MPL study as the goal is to determine the performance improvement under flooded conditions.



**Figure A.2: Photos of (a) a full size MEA and (b) a masked MEA in TP50**

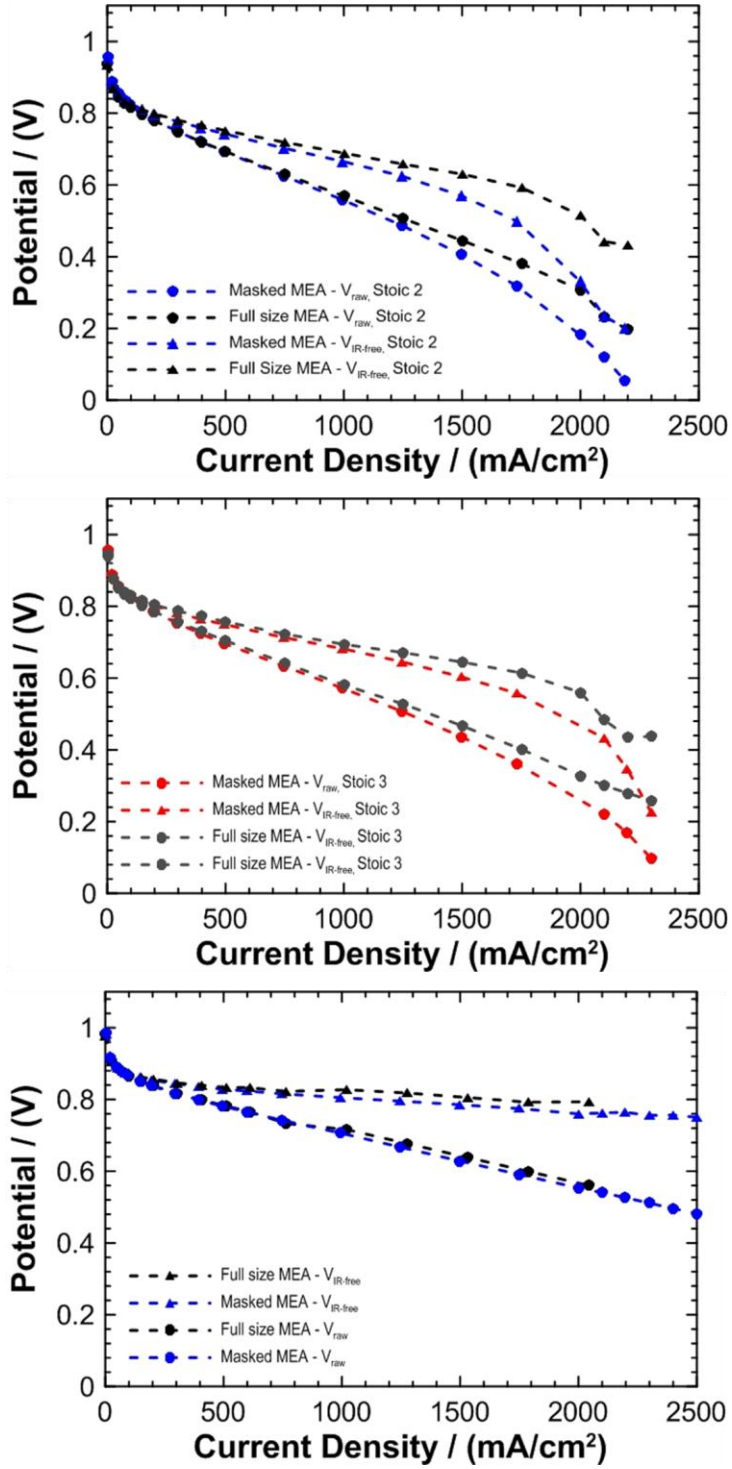
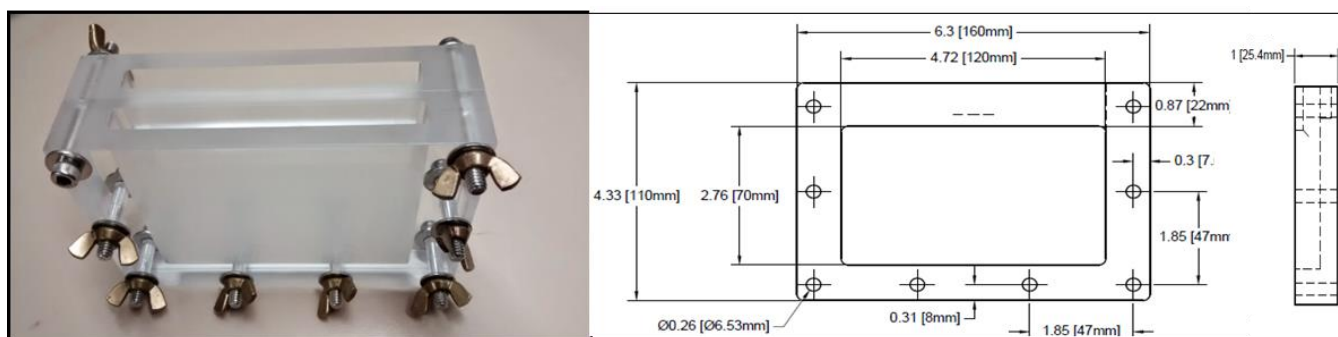


Figure A.3: Performance comparison of the masked MEA (14 cm²) vs. full size MEA (49 cm²) with TP50 cell: (a) with  $\lambda_c = 2$  on air, (b) with  $\lambda_c = 3$  on air, and (c) with  $\lambda_c = 2$  on oxygen.

#### A.4 Electroless Deposition Cell

The deposition cell was made of a chemically inert material such as PTFE or polycarbonate and sealed with a number of bolts and nuts to ensure no leakage from the cell during deposition. A clear cell is suggested as to enable monitoring of the electroless Pt layer synthesis. A photograph and the dimensions of the deposition cell are presented in Figure A.4. This deposition cell consists of two separated compartments, which can be tightly sealed if a membrane is placed in between.



**Figure A.4: Electroless deposition cell photo, and (b) engineering drawing of the cell constructed from polycarbonate used for electroless deposition with an exposed area of 11 cm × 7 cm.**

## A.5 Water Diffusion

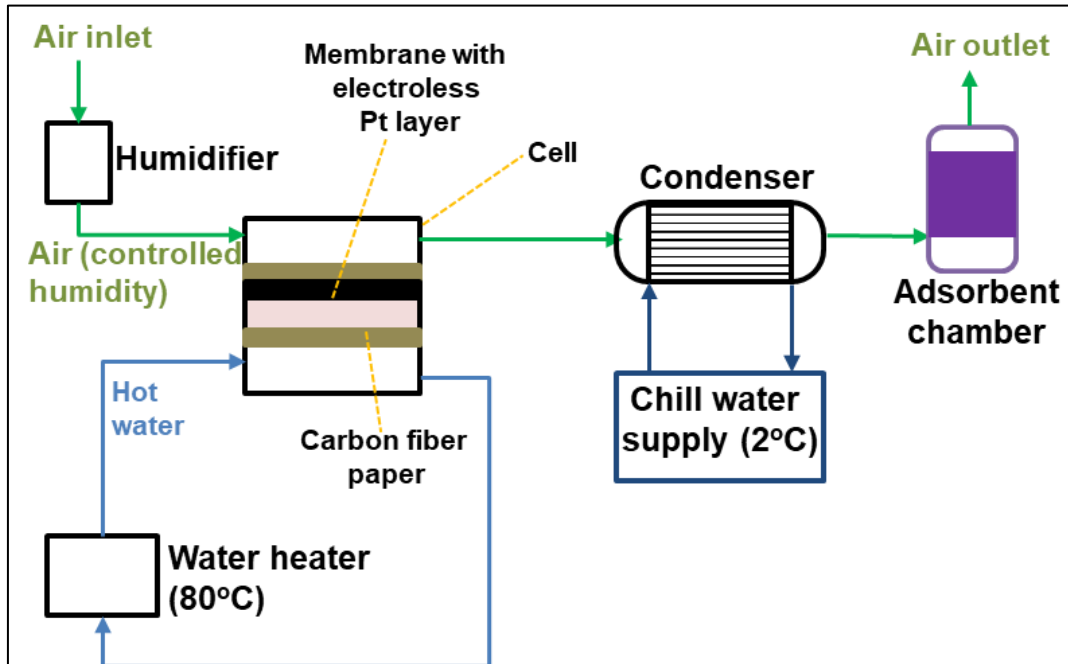


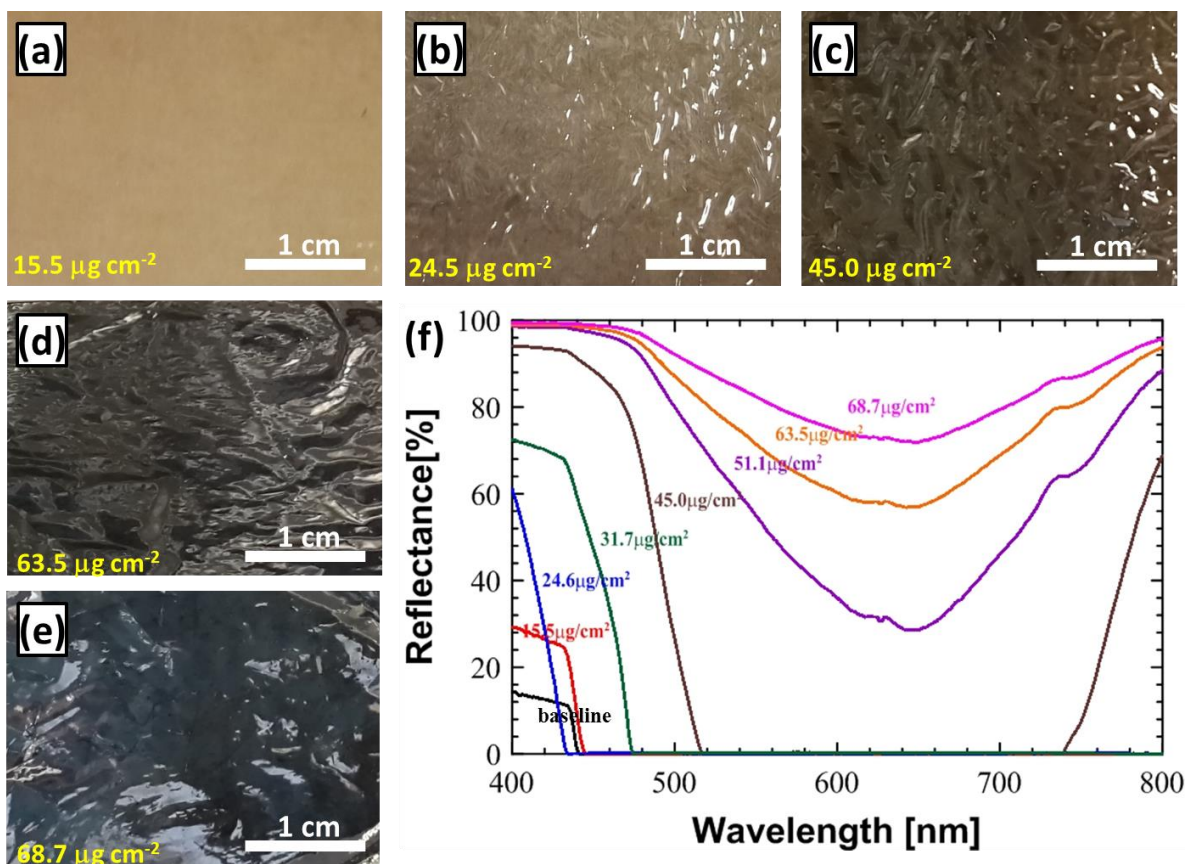
Figure A.5: Schematics and process flow diagram of the water diffusion experiment

## Appendix B - Supporting Information for Electroless Pt Study

### B.1 Optical Reflectivity

As the Pt loading increases, the color of the platinized membranes transforms from a lighter brown to a darker brown to almost black and then finally to a glossy black-gray (Figure B.1). The transformation from light brown to a glossy black-gray at a loading of  $63.5 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  could suggest a near monolayer coverage, indicating strong Rayleigh scattering and high optical density [63]. This was supported by the reflectance spectra measured in the 400 - 800 nm range of wavelengths. Reflectance measurement in this visible light spectrum shows that the electrolessly deposited membranes with loadings higher than about  $52 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  exhibit significant reflectivity compared to the samples with loadings below about  $52 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  which do not reflect for most of the region of the visible light spectrum. The reflectivity of the electrolessly deposited membrane increases with increased Pt loading and reaches ~80% for visible light at the near saturated Pt layer achieved in the membrane. The improved reflectivity of a metallic polymer has been linked to its enhanced conductivity [171,172], i.e., higher conductivity for electrolessly deposited membranes with higher loadings.





**Figure B.1: Physical appearance of the electrolessly-deposited membrane with different Pt loadings: (a) 15.5, (b) 24.6, (c) 45.0, (d) 63.5, (e) 68.7  $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ , and (f) profile of reflectance vs. Pt loading with a baseline of blank membrane**

## B.2 Ionic and Electronic Conductivity Measurements

Figure B.2a shows the in-plane electronic conductivity vs. the electroless Pt loading. The conductivity of the platinized membranes studied here can be classified into three groups: I) membranes with electroless loadings  $< 35 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  exhibiting low in-plane conductivity ( $< 10 \text{ mS cm}^{-1}$ ), II) membranes with electroless loadings of  $35 - 60 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  in a transition region exhibiting a rapid increase of conductivity with increased loading ( $10 \text{ mS cm}^{-1}$  to over  $1 \text{ S cm}^{-1}$ ), and III) membranes with electroless loadings of  $> 60 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  exhibiting significantly higher in-plane conductivity ( $\sim 4 - 7 \text{ S cm}^{-1}$ ). The very low conductivity at the loadings below  $32 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  suggests that inter-particle connectivity was very low for the platinized membranes in this

region. The inter-particle connectivity is significantly improved for loadings greater than  $32 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  and reaches a constant value ( $\sim 4 - 7 \text{ S cm}^{-1}$ ) for loadings greater than about  $60 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ . Enhancement of Pt grain connectivity leads to improved electron transfer pathways and leads to an apparent maximum conductivity value ( $\sim 4 - 7 \text{ S cm}^{-1}$ ) for loadings higher than  $60 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  indicating that Pt grains are essentially almost all connected together. The overall improvement in the electronic conductivity observed here is about three orders of magnitude.

The protonic conductivity of the Pt-deposited membranes under dry condition at room temperature, however, decreases with increased levels of Pt loading (Figure B.2b). Over the range of Pt loadings studied here ( $12 - 70 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ) the protonic conductivity reduces from 0.7 to 0.1  $\text{mS cm}^{-1}$  or a factor of  $7\times$ . The reduced through-plane proton conductivity may result from formation of denser Pt clusters at the membrane sub-surface which impedes the transfer of protons across the membrane.

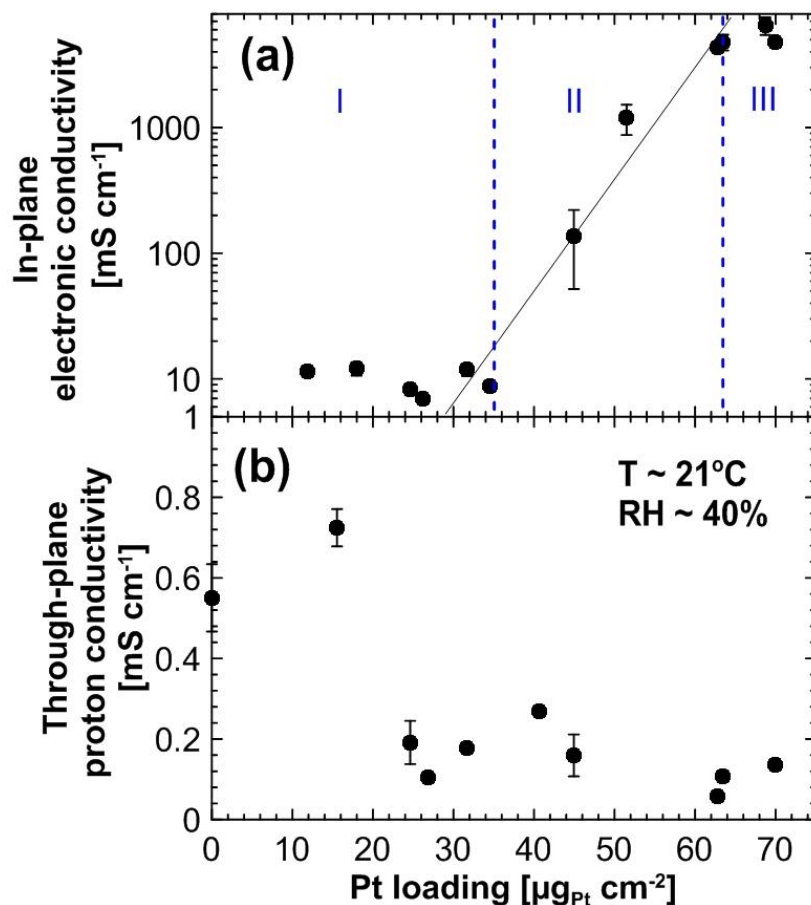


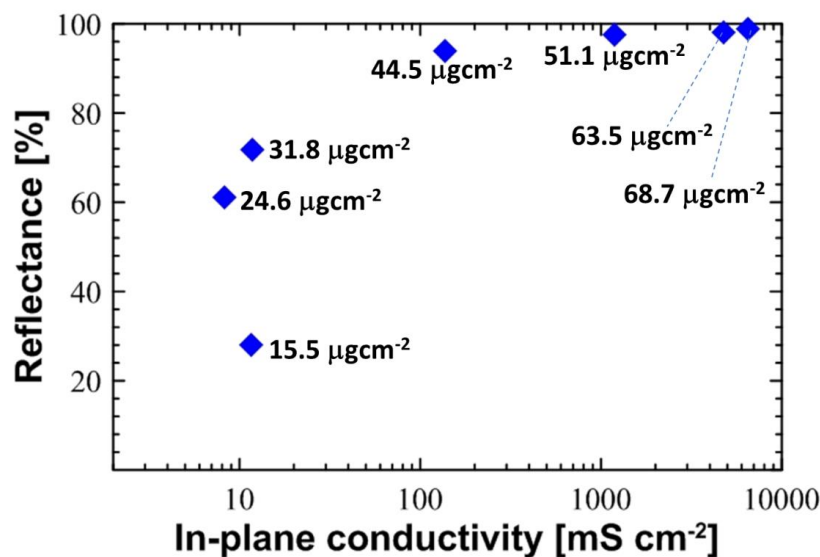
Figure B.2: (a) In-plane volume resistivity, and (b) through-plane proton conductivity of the platinized membrane vs. Pt loading. The vertical error bars in (a) indicate the standard deviation from nine different points across the sheet, and in (b) indicate the standard deviation from three different measurements.

### B.3 In-plane Conductivity and Optical Reflectivity

A spectrophotometer (Ocean Optics, USB2000 + UV-Vis, range: 200-850 nm) equipped with R-400-7-UV-Vis optic fibers (Ocean Optics, fiber diameter = 400  $\mu\text{m}$ , length = 2 m) and a deuterium halogen source (DH-2000 BAL, range: 230 – 2500 nm) was used to determine the optical reflectance of membranes with an electroless Pt layer. The calibration for reflectance was conducted with an aluminum-mirror-with-fused-silica standard (Ocean Optics, STAN-SSH). All absorbance spectral measurements were carried out in the wavelength range of 400 - 800 nm and

at room temperature (21°C) with no humidification. The Pt-deposited side of the membrane samples was held flat underneath the reflector probe (Ocean Optics, RPH-1, probe size = ¼”) and the samples were illuminated at an angle of 90°. The corresponding absorbance spectrum was recorded when steady-state conditions were reached (usually about 10 s after the beginning of illumination).

Figure B.3 shows the correlation of the in-plane electronic conductivity and reflectance for different electroless Pt loadings. The transformation from light brown to glossy black-gray at reflectance values higher than 80% (from a loading of 45.0 to 68.7  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ) suggests a near monolayer coverage which is closely related to the enhanced Pt grains connectivity. Here, the saturation or enhanced Pt grain connectivity is demonstrated by an increase of in-plane conductivity by almost three orders of magnitude from  $<10 \text{ mS cm}^{-1}$  to  $\sim 7000 \text{ mS cm}^{-1}$ . It is therefore clear that the Pt interparticle connectivity is improved as the loading increases. Martens et al., similarly, demonstrate an increase in optical reflectivity as the Pt film in the membrane has grown to near monolayer coverage [63].



**Figure B.3: In-plane conductivity vs. reflectance of electroless Pt samples with different loadings in the visible light spectrum ( $\sim 400 - 600 \text{ nm}$ ).**

#### B.4 Pt Grains Interconnectivity Modeling Using a Simple Geometric Approach

It is instructive to consider a number of different possibilities for the Pt grain growth and utilization as the Pt loading ( $M_{\text{Pt-grain}}$ ) increases (Table B.1). Each case (*A - F*), represents an example of increasing  $M_{\text{Pt-grain}}$  in the membrane. The increased  $M_{\text{Pt-grain}}$  could result from: i) growth of new grains with dimensions similar to the existing grains (*Case A*, increasing  $N_{\text{Pt-grains}}$ ), ii) growth on top of the existing grains with no grain coalescence of grains (*Cases B – D*, constant  $N_{\text{Pt-grains}}$ ) or iii) grain growth and coalescence (*Cases E – F*, decreasing  $N_{\text{Pt-grains}}$ ). *Case A* corresponds to a constant Pt grain size ( $r_{\text{Pt-grain}}$ ) and  $Pt_{\text{utilization}}$ , hence,  $M_{\text{Pt-grain}}$  is simply proportional to  $N_{\text{Pt-grains}}$ . In all other cases increasing the  $M_{\text{Pt-grain}}$  leads to an increased  $r_{\text{Pt-grain}}$  and would be proportional to  $V_{\text{Pt-grain}} \times N_{\text{Pt-grains}}$ . For *Cases C - F* we consider a number of different power laws dependencies of  $Pt_{\text{utilization}}$  on the  $r_{\text{Pt-grain}}$  for simplicity. *Cases C* and *E* correspond to cases where the increase in  $r_{\text{Pt-grains}}$  leads to more connected particles and  $Pt_{\text{utilization}}$  is assumed to be proportional to a linear increase in  $r_{\text{Pt-grain}}$ . For *cases D* and *F*, the increase in  $r_{\text{Pt-grains}}$  is assumed to increase the  $Pt_{\text{utilization}}$  proportional to the square of  $r_{\text{Pt-grain}}$ . From the variation of three independent variables, one can then obtain the dependency of  $M_{\text{Pt-grains}}$  and ECSA as dependent variables on the  $r_{\text{Pt-grain}}$  using the equation below:

$$\text{ECSA} = \frac{N_{\text{Pt-grains}} \times A_{\text{Pt-grain}}}{W_{\text{Pt}}} \times Pt_{\text{utilization}} = \frac{N_{\text{Pt-grains}} \times A_{\text{Pt-grain}}}{N_{\text{Pt-grains}} \times \rho_{\text{Pt}} \times V_{\text{Pt-grain}}} \times Pt_{\text{utilization}}$$

**Table B.1. Description of model variables and their impact on  $M_{\text{Pt-grain}}$** 

| Case | Independent Variables             |                       |                          | Dependent Variable    |
|------|-----------------------------------|-----------------------|--------------------------|-----------------------|
|      | $N_{\text{Pt-grains}}$            | $r_{\text{Pt-grain}}$ | $P_{\text{utilization}}$ | $M_{\text{Pt-grain}}$ |
| A    | increasing                        | constant              | constant                 | $\propto N$           |
| B    | constant                          | increasing            | constant                 | $\propto r^3$         |
| C    | constant                          | increasing            | $\propto r$              | $\propto r^3$         |
| D    | constant                          | increasing            | $\propto r^2$            | $\propto r^3$         |
| E    | decreasing<br>( $\propto 1/r^2$ ) | increasing            | $\propto r$              | $\propto r$           |
| F    | decreasing<br>( $\propto 1/r^2$ ) | increasing            | $\propto r^2$            | $\propto r$           |

Figure B.4 shows the schematics of all the possibilities considered in Table B.1. For each case we use the  $r_{\text{Pt-grain}}$  dependency of Pt mass loading and the ECSA in order to plot the expected behavior of ECSA on the  $M_{\text{Pt-grains}}$ . The figures also show the evolution of the Pt films through growth and/or formation/coalescence of Pt grains.

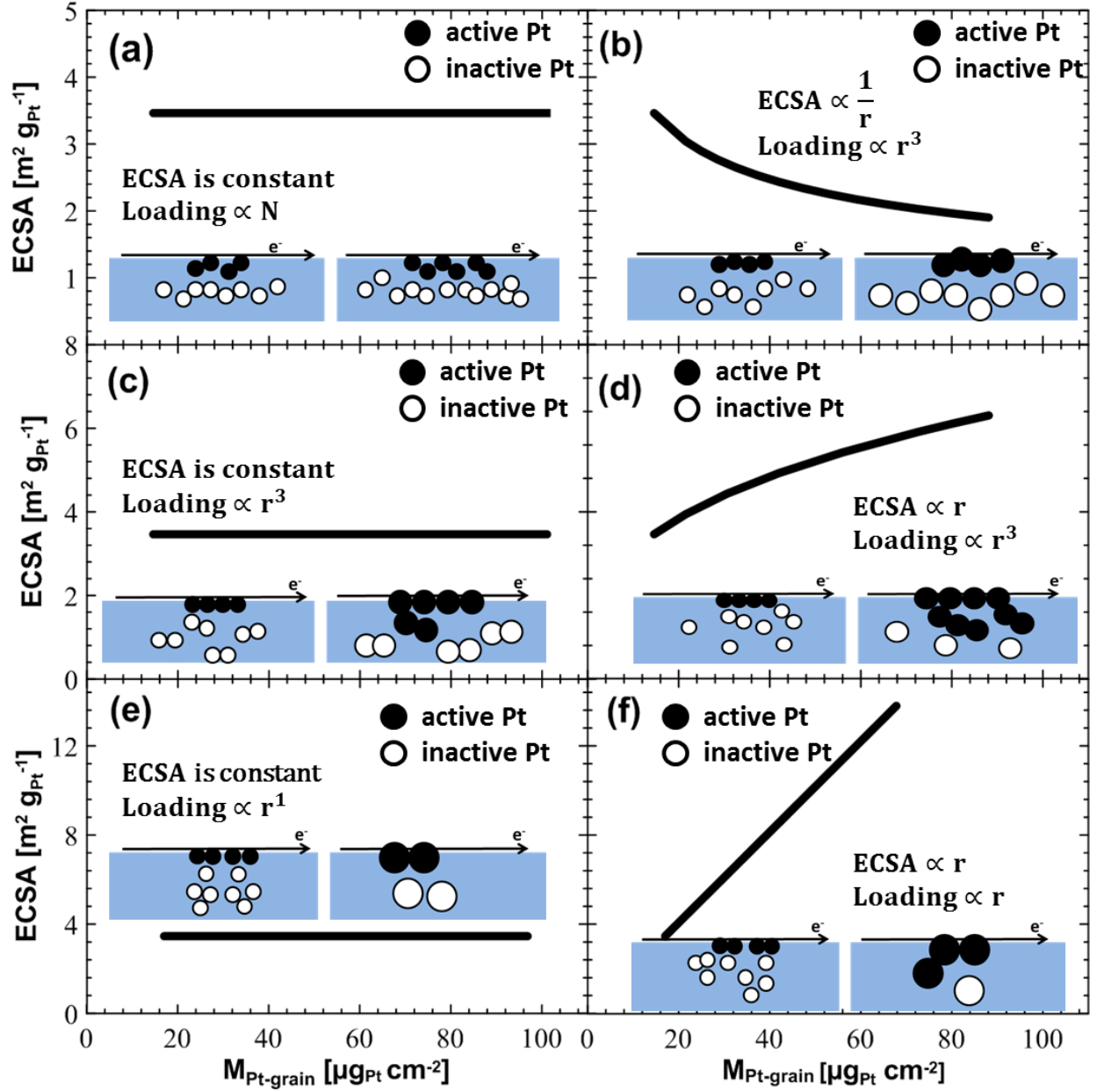


Figure B.4: Modelling the impact of Pt loading variables on  $M_{\text{Pt-grain}}$  and ECSA: (a) constant  $Pt_{\text{utilization}}$  and an increasing number of grains, (b) constant number of grains and increasing particle size, (c) constant number of grains, increasing grain size, and increasing Pt utilization linearly with size, and (d) constant number of grains, increasing grain size and increasing Pt utilization quadratically with size, (e) similar to (c) but with decreasing number of grain quadratically with size, and (f) similar to (d) but with decreasing number of grains quadratically with size.

## B.5 Proton Conductivity

The platinized membrane structure also provides more sites for hydrogen-oxygen recombination in between the two electrodes to suppress the undesired hydrogen crossover and produce water inside the membrane, which improves membrane hydration (Figure B.5).

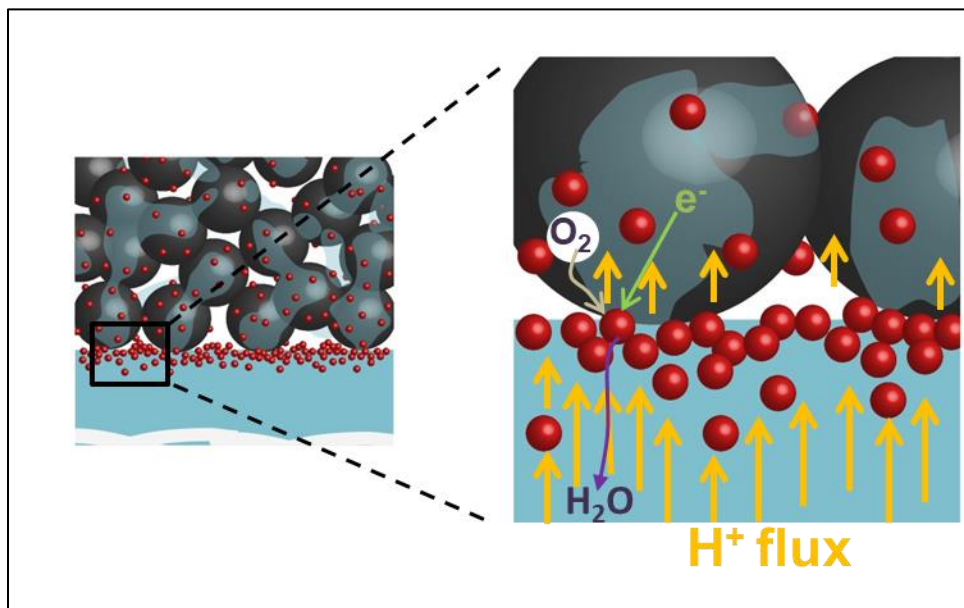


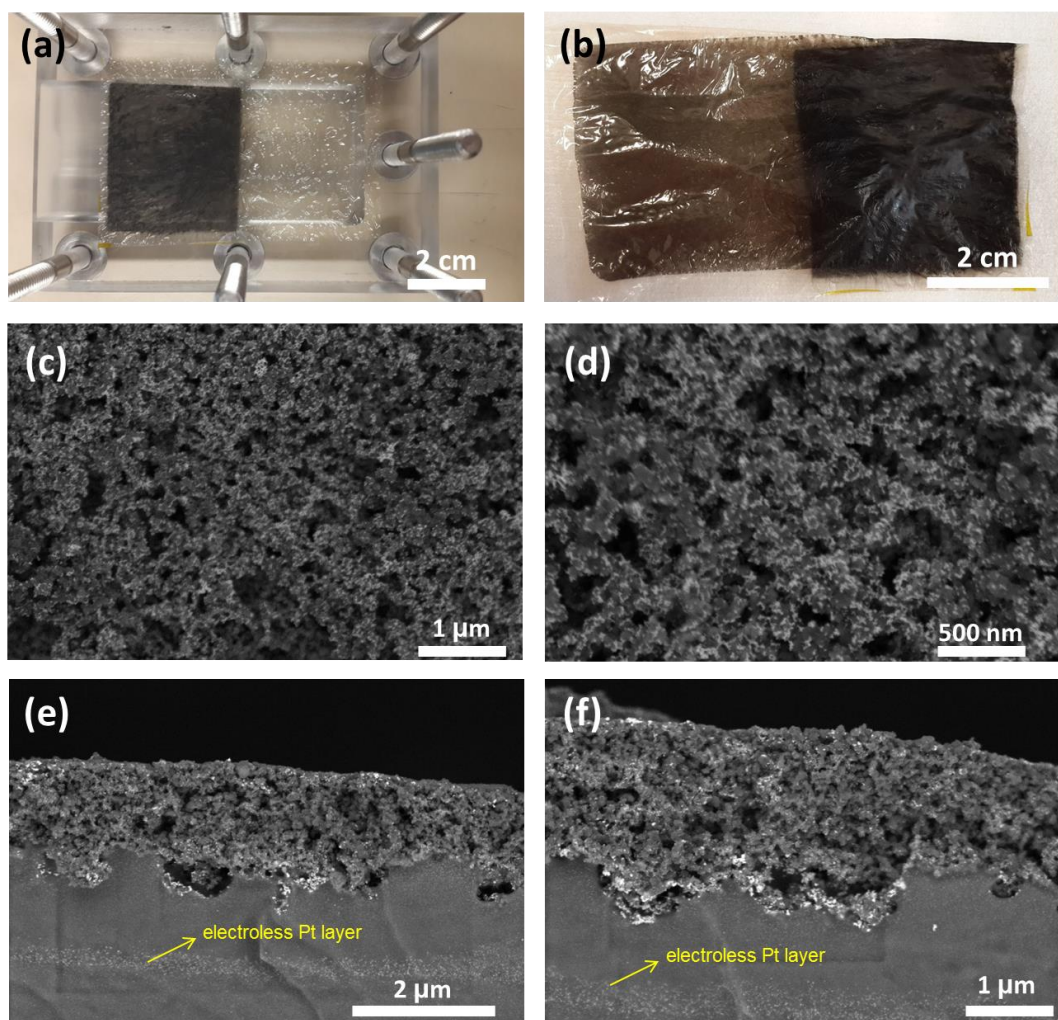
Figure B.5: Schematic of electroless Pt layer and the reduction of proton flux by this layer

## B.6 Electroless Pt on a Carbon Coated Membrane

An initial attempt to electrolessly deposit Pt on a carbon coated membrane was conducted by spraying a thin layer of carbon onto the membrane followed by the regular electroless Pt deposition procedure as explained in the experimental section. Half of the area of the membrane was not exposed to carbon layer during spraying to enable direct comparison with a regular platinized membrane structure (Figure B.6a and b). SEM images of the surface of the carbon layer shown in Figure B.6c and d indicate that the electroless Pt was deposited evenly throughout the surface. However, the concentration of the Pt on the surface is apparently high, which may result in a lower Pt concentration in the carbon layer and the membrane subsurface. Figure B.6e



and f further reveal that the electroless Pt particles were deposited deeper inside the membrane with only a small fraction at the membrane|carbon interface. The thickness of the carbon deposited in this study ( $\sim 1.5 \mu\text{m}$ ) might be too thick for this purpose and is responsible for the limited penetration of the Pt particles into the carbon layer and the membrane. Based on this initial attempt, a further investigation needs to be done to improve the control of the resulting structure with a modification in the synthesis parameters.



**Figure B.6:** (a) Photo of the partially carbon coated membrane before deposition, and (b) after deposition; (c-d) SEM images of the top surface of the carbon coated membrane after deposition; (e-f) SEM images of the cross-sectional of the carbon coated membrane after deposition.

## Appendix C - Carbon Black Properties

The properties of the carbon black materials used in this thesis obtained from relevant literature are summarized in Table C.1. From the data presented here, the correlation between surface area and average pore diameter is observable. The surface area tends to decrease with the increase of average pore diameter.

**Table C.1. Summary of surface area and pore diameter of several MPLs**

| MPL Material          | Surface Area<br>(m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup> | Average Pore<br>Diameter<br>(nm) <sup>a</sup> | Maximum Pore<br>Diameter (nm) <sup>a</sup> | Ref   |
|-----------------------|----------------------------------------------------------------|-----------------------------------------------|--------------------------------------------|-------|
| Vulcan XC72R          | 18.1                                                           | 30                                            | -                                          | [173] |
| Shawinigan Black AB50 | 13.9                                                           | 63                                            | -                                          | [173] |
| Black Pearls 3700     | 7.5                                                            | 86                                            | -                                          | [173] |
| AB Denka Li100        | 35.5                                                           | -                                             | 67                                         | [82]  |
| AB Denka Li400        | 19.6                                                           | -                                             | 328                                        | [82]  |

<sup>a</sup> Measured as a layer property with mercury intrusion porosimetry.

## Appendix D - MEA Assembly

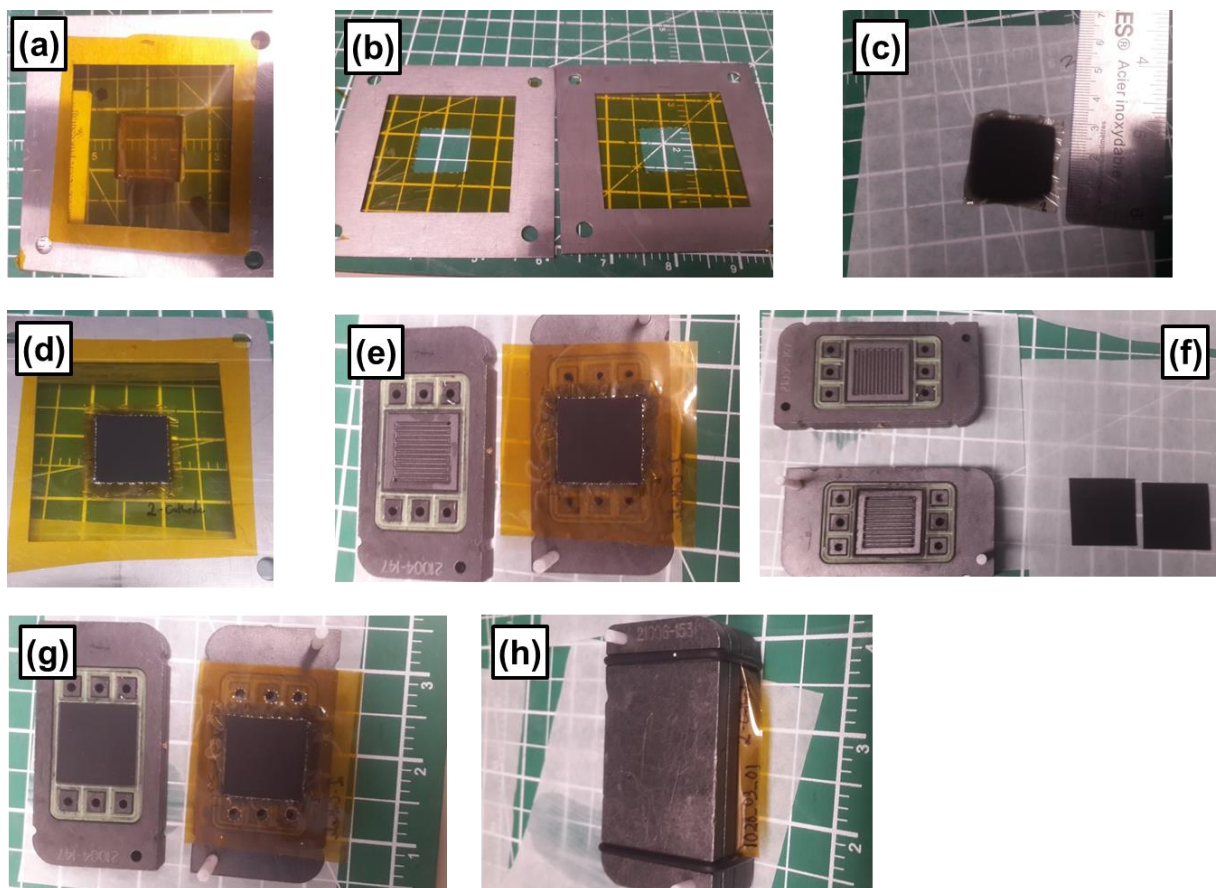
**Step 1:** The assembly of the cell for fuel cell testing consists of several steps: (i) CCM preparation and assembly, (ii) MPL/GDL preparation and assembly, and (iii) cell assembly.

i. CCM preparation and assembly:

- Two pieces of Kapton are cut and taped to the hollow Kapton frame (Figure D.1a).
- A window with the size of the active area is cut at the center of each Kapton (Figure D.1b).
- The CCM is cut with a size of little larger than the active area (Figure D.1c).
- The CCM is sealed by the pair of the Kapton tapes, and the sealed CCM is cut off from the frame (Figure D.1d).
- Holes aligned with the holes on the flow field were made by using a hole puncher (Figure D.1e)
- Label the side as anode and cathode on the Kapton.

ii. MPL/GDL preparation and assembly: For the GDL/MPL preparation cut the GDL/MPL to fit the size of the inner side of the gasket on the flow fields. The MPL side should be facing the CCM (Figure D.1f and g).

iii. Cell assembly: To assemble the cell, place each GDL/MPL on each half-side of the cell. Then, place the sealed CCM on one of the half-side of the cell. Combine the two half-side of the cell together with alignment pins; seal the cell with O-rings on both sides (Figure D.1h)



**Figure D.1: (a-h) Steps of MEA assembly with TP5**

**Step 2:** Place the cell in the test stand and apply pressure to compress the cell by turning on the  $N_2$  gas line into the cell bladder. Load the fuel cell assembly between the bipolar plates and connect all appropriate voltage leads, temperature probes, inlet/outlet lines etc.