Proton Conduction and Kinetics Studies
in Proton Exchange Membrane Fuel Cell Cathodes

by

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Submitted in Partial Fulfillment
of the
Requirements for the Degree
Doctor of Philosophy

Supervised by
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University of Rochester
Rochester, New York

2009
Dedication

To my husband, Jiahui, and our daughter, Shangqing
-for the happiness and love they give to me
Curriculum Vitae

The author was born in Jimo, Shandong Province, China on October 12, 1976. In the Fall of 1995, she attended the Dalian University of Technology and graduated with a Bachelor of Engineering degree in Corrosion and Protection in 1999 and a Master of Engineering degree in Applied Chemistry in 2002. During this time span, she was educated in the field of electrochemistry with a focus on corrosion, and finished with a thesis titled: *Influences of Sulphate-Reducing Bacteria on the Corrosion Behavior of Carbon Steel*. In 2005, she received a Master of Science degree in Chemical Engineering at the University of Connecticut with a thesis titled: *Organic/Inorganic Composite Membranes for High Temperature PEM Fuel Cells*. Then, in the Fall of 2005, she was admitted to the Department of Chemical Engineering at the University of Rochester to pursue a PhD degree, with a focus on PEM fuel cells and electrochemistry, under the supervision of Prof. Jacob Jorné. In collaboration with General Motors, she conducted her research in the Electrochemical Energy Laboratory (then Fuel Cell Research Lab), General Motors, in Honeoye Falls, NY since March 2006. In 2007 and 2008, she received an *Electrochemical Society Travel Grant Award* for work presented on proton conduction in PEM fuel cell electrodes. In 2008, the author was awarded the *Dr. Bernard S. Baker Award for Fuel Cell Research* as the 1st place winner, presented at the Fuel Cell Seminar in Phoenix, Arizona. In 2009, she received the *Gordon Research Conference (Fuel Cells) Chair Funding* and acted as activity chair coordinator in the conference.
Publications and Conference Presentations


Acknowledgements

I owe so many acknowledgements to people who have helped me in every respect. Foremost, I would like to thank my advisor, Professor Jacob Jorné. I have always felt so lucky to be his student and to pursue my PhD under his supervision. What I learned from him is not only electrochemistry and proper research attitude, but also how to be a good person. I enjoyed every minute of our conversations on both research and sports. I particularly thank Prof. Jorné for setting up the collaboration with General Motors Fuel Cell Activities, giving me an unforgettable experience within my PhD study. I am so blessed to have had the special opportunity of being educated in combined academic and industrial environments. I thank the Department of Chemical Engineering for the first year’s financial support. I also thank the ladies in our CHE Department office for their kind and considerate support.

At GM, first of all, the financial support is gratefully acknowledged. I owe numerous thanks to a group of great people who provide me with tons of help, particularly Mark Mathias, Wenbin Gu, Daniel R. Baker, Chunxin Ji, and Hubert Gasteiger. Mark oversees my whole study and projects. I thank him particularly for his contribution to Chapter 7 and insightful discussion of other Chapters. Wenbin has instructed me on a daily basis. His help with my research is beyond the words. Danny, a brilliant mathematician and modeler in AC impedance, provided his unselfish help with the impedance model, allowing my data to be effectively translated to meaningful results. Chunxin’s expertise in material science has particularly benefited the electrode material related work in Chapters 2, 3 and 5. I would like to acknowledge and thank Hubert A. Gasteiger for all of his help with my research and for his contribution to Chapters 2, 3, 5 and 6. Though he
left GM in 2007, he has remained actively engaged in my research. My special thanks go to him for reading, correcting my papers, and providing me with his insightful viewpoints. Their professionalism has inspired me to work harder in order to approach their expertise. I extend my acknowledgement to Junliang Zhang, specifically for his contribution to Chapter 7, to Ruichun Jiang, for his helpful discussion in membrane related sections, to Mike Murphy, for teaching me to use the AC impedance and for all our hard work together, and to K.C. Neyerlin, for his help when I started in the lab. I also wish to thank Eric Thompson, Vic Liu, Paul Yu, Yeh-hung Lai, Abel Chuang, Jingxin Zhang, Rohit Makharia, Fred Wagner, for the generous sharing of their time with me on technical discussions. I wish to thank Tom Trabold for reviewing my reports. I would also like to thank Paul Lubberts, Mike Scozzafava, and Matt Dioguardi for helping make MEAs, Tim Fuller for casting membranes used in membrane resistance measurement, Ted Gacek for the SEM imaging, and Robert Moses who provided strong support on the experimental setup and instrument maintenance. I would also like to acknowledge Travis Downs, Tracey Paige, Peter Harvey, and Joseph Kubik in the small scale cell testing lab for their help on cell running. I also wish to acknowledge Stacy Downs, Heidi Viterise, Paul Gregorius, and Mike Flanagan in the clean room.

I would like to thank all of my friends for their friendship over the years. Finally, I would like to thank my husband and our daughter for the happiness and love they give to me and my parents and in-laws for their unselfish support in all aspects of my life.
Abstract

The dominant voltage loss in proton exchange membrane (PEM) fuel cells is associated with the cathode and includes oxygen reduction reaction (ORR), proton transport in the ionomer phase, and oxygen transport. The proton transport within the ionomer can result in significant voltage loss, especially under dry conditions and/or at high current densities. The proton resistance in the cathode is determined by AC impedance in a H₂/N₂ cell, and is analyzed by a 1-D transmission-line model assuming the capacitance and resistance are uniformly distributed through the entire electrode thickness. The electrode proton resistivity is found to be independent of the electrode thickness and the carbon-support platinum %wt, as it strongly depends on the ionomer-to-carbon weight ratio (I/C) and relative humidity (RH). A critical point exists for the ionomer network in the electrode, beyond which point the ionomer tortuosity is around 1, while below the point, the tortuosity increases dramatically. The effects of the electrode ingredients on the proton resistivity and cell performance are investigated by varying the ionomer equivalent weight and the Pt-dispersed carbon supports. The density of the sulfonic acid groups in the cathode determines the proton resistivity and hence the cell performance. The proton resistivity, normalized by the ionomer bulk resistivity depends intrinsically on the volumetric ratio of ionomer-to-carbon (I/C), and is also affected by the porosity and roughness of the carbon support as a portion of the ionomer is absorbed by the carbon. The proton resistivity increases with increasing carbon surface area though improving ORR kinetics. The effect of relative humidity (RH) on ORR kinetics is determined to be small. The kinetics of Pt oxidation by water and the effects of potential, temperature, RH, and prior exposure to oxygen environments are studied and characterized by a surface coverage model. The water
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Chapter 1

Introduction to Proton Exchange Membrane (PEM) Fuel Cells

A fuel cell is an electrochemical conversion device that converts chemical free energy to electricity without the limitation of the Carnot efficiency. In contrast to a battery, a fuel cell is an open operating system which produces electricity from externally supplied fuel and oxidant.

In the over 150-year history of fuel cells, various types of fuel cells have been developed. Generally, fuel cells are characterized by the type of electrolyte: solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), and alkaline fuel cell (AFC). The conducting ions for SOFC, MCFC and AFC are anions, formed on the cathode and transported toward the anode. On the other hand, in PEMFC, DMFC and PAFC, proton (H⁺) is the conducting species transported through the electrolyte from the anode to the cathode and the H⁺ conductivity strongly depends on the water activity. Perry and Fuller present an excellent review on the significant development of fuel cells in the past century, summarizing the applications, advantages and disadvantages of each type of fuel cell. Cost and durability are the two major hurdles for all fuel cells.

The H₂-powered PEM fuel cell is perceived as an alternative to a conventional internal combustion engine for automotive applications, due to its fast start-up, low operating temperature, high fuel efficiency, and environmentally friendly advantages.
Recently, several auto makers have introduced H2-fed fuel cell vehicles on the road. However, some concerns, i.e., catalyst and membrane’s cost and durability, catalyst activity, membrane proton conductivity, and water management, still exist. In order to make the fuel cell vehicle affordable and durable, further work needs to be done to improve each of the above mentioned aspects. In the following sections, further description of PEM fuel cells and the motivation for this work are presented.

1.1 PEM FUEL CELLS

A PEM fuel cell distinguishes itself by operation at low temperature (~80°C) using a polymer membrane as the electrolyte. A schematic of a single H₂/O₂ PEM fuel cell is shown in Figure 1.1, where the half reactions, the path of each charge carrier (H⁺, e⁻), and reactants and product are presented.
As shown in Figure 1.1, a cell is generally composed of a proton exchange membrane sandwiched by an anode and a cathode. The assembly of these three parts is termed membrane electrode assembly (MEA), which is the heart of a single PEM fuel cell. The MEA is further sandwiched between two diffusion media (DM) and two flow fields (FF); the latter also act as a current collector on each side. At the anode, H₂ is fed and transported via the FF and DM to the catalyst layer, where H₂ is oxidized to form protons and electrons. The protons are transported across the membrane carrying H₂O toward the cathode, and the electrons leave via the current collector and the external wire toward the cathode. At the cathode, O₂ is fed into the FF, diffuses toward cathode catalyst layer, and
reacts with $H^+$ and $e^-$ to form $H_2O$. Finally, produced water travels away from the catalyst layer to either the cathode FF or through the membrane to the anode FF. During this process, two half reactions are involved:

$$\text{Hydrogen oxidation reaction (HOR) on anode: } H_2 \rightarrow 2H^+ + 2e^- \quad E^0 = 0V \quad [1.1]$$

$$\text{Oxygen reduction reaction (ORR) on cathode: } \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^0 = 1.23V \quad [1.2]$$

and the total cell reaction is

$$\frac{1}{2}O_2 + H_2 \rightarrow H_2O \quad E^0 = 1.23V \quad [1.3]$$

where $E^0$ is the standard equilibrium potential.

Each component shown in Figure 1.1 plays a unique role in the cell operation. In what follows, further details on each component are described.

1.1.1 PEM fuel cell components descriptions

**Membrane:** The membrane needs to exhibit good proton conduction, zero electron conduction, and very low permeability for $H_2$ and $O_2$. Typically, PEM fuel cells operate at ~$80^\circ$C under a pressurized and humidified atmosphere and they have to be chemically and mechanically durable to survive these conditions. For PEM fuel cells, the commercially mature membrane is a perfluorosulfonic acid (PFSA) membrane, such as Nafion® (DuPont), Aciplex® (Asahi Chemical), and Flemion® (Asahi Glass), which have a similar structure and conduct protons via sulfonic acid groups (-SO$_3$H). Nafion® was
discovered in the late 1960s by Walther Grot of DuPont.\textsuperscript{2, 3} It is considered the benchmark material. The proton conductivity of Nafion\textsuperscript{®} strongly depends on the molecular equivalent weight (EW, \(g_{\text{polymer}}/\text{molSO}_3\)), also termed the ion exchange capacity (IEC). The EW is equivalent to the reciprocal of IEC multiplied by 1000. Lower EW or higher IEC generally represent higher proton conductivity.

Figure 1.2a shows an example of general chemical structure of Nafion\textsuperscript{4}, a polytetrafluoroethylene (PTFE)-like backbone connected with a perfluorocarbon unit, and a -SO\textsubscript{3}H group. For a Nafion\textsuperscript{®} membrane with EW of 1100, \(n\) is about 7.\textsuperscript{3} Due to the unique composition of Nafion\textsuperscript{®}, its structure is rather complex. Researchers proposed several structure models attempting to describe how the ionic groups aggregate within the membrane represented by the well-known Gierke Cluster Network Model\textsuperscript{5} as shown in Figure 1.2b. It is believed that within the membrane, clusters with \(\sim 40\text{Å}\) diameter are formed by inverted-micelles assembled by the -SO\textsubscript{3}H-ended side chains, and connected with neighbor clusters by pores or channels of \(\sim 10\text{Å}\) diameter. These channels are regarded as the path for the transport of water and proton H\textsuperscript{+} within the membrane.
Though Nafion®-like membranes are considered the first choice in PEM fuel cell applications, this type of membrane is quite expensive. In addition, they are prone to degradation due to the formation of the by-product peroxide formed by H₂ and O₂. To approach the cost and durability target, great effort is invested in the development of non-perfluorinated hydrocarbon-based membranes, which unfortunately have their own drawbacks, such as very poor conductivity under subsaturated conditions. To address all these issues, more effort is needed.

**Electrodes:** The electrodes, especially the cathode for the oxygen reduction reaction (ORR), are the key component in a fuel cell, determining the cell performance. Generally, the electrode is composed of catalysts, proton conductive materials (e.g.,
Nafion® ionomer), and electronic conductive materials (e.g., carbon) The most commonly used catalyst for the ORR is Pt or alloyed Pt nanoparticles dispersed on carbon support materials. However, these precious metal catalysts are very expensive and in limited supply. Two research directions are currently being pursued: 1. The development of new catalysts with higher ORR catalytic activity, better durability, and lower cost; 2. Design and optimization of the electrode in order to reduce the amount of catalyst.

Recently, Gasteiger et al 6 and Payne et al 7 overviewed current strategies aiming to solve the issues of catalyst cost and durability. There are two pathways toward these goals: greatly increase catalytic activity of the precious metal or replace a Pt-based catalyst with a non-precious metal ORR catalyst. Catalyst activity can be enhanced by altering the catalyst structure (size and shape), and through Pt alloying. A recent example is the 3M–developed, nanostructured thin film (NSTF) Pt-alloy catalyst for ORR, which demonstrates improved activity and durability in fuel cell tests. 8 Another strategy to decrease the catalyst cost is using non-precious metal catalysts. Recently Lefevre et al 9 have demonstrated that a novel Fe/N/C non-Pt based catalyst matches the activity of Pt/C, however, durability tests show that after 100 hours the current density decreased by ~50% at the same potential, requiring more effort to improve its durability in the future.

The integration of catalysts with other fuel cell components, given the state-of-the-art catalyst, is also of great importance. As mentioned in the beginning of this section, the electrode is usually made with carbon supported catalyst and proton conducting material, such as PFSA ionomer dispersions. Other types of electrodes do not have ionomer, for example, NSTF, but at dry conditions, its performance is lower than conventional electrodes. All electrodes reported in the thesis are made with carbon supported catalyst.
To increase the performance, ionomers with higher proton conductivity are highly desirable. The electrode performance depends on the quality of the ink, which depends on its catalyst content and the ionomer and solvent compatibility, which determines ink viscosity and coatability. Ink is usually prepared by dispersing the carbon supported catalyst, the ionomer and the desired solvent together. Subsequently, the ink is either applied to the membrane or to the diffusion media (DM). The former is called catalyst coated membrane (CCM), and the later is called catalyst coated diffusion media (CCDM). CCDM is easier to assemble, especially at the stack scale, but the Pt loading control is less accurate than CCM. In this thesis, the CCM architecture is adopted, where the ink is applied to the membrane.

**Diffusion Media:** On each side of the MEA, a thin DM is pressed against the electrode. The purpose of the DM is to help the transport of reactant gas to the electrode from flow field (FF), to redistribute the reactant over the electrode, and to protect the MEA as well as to remove the product water from the electrode to the FF. The DM has to be electronically and thermally conductive to provide electrons and heat conduction pathways to and away from the electrode. From the cell performance point of view, the DM needs to effectively meet the above requirements and to minimize its voltage drop. Based on the above mentioned requirements, the DM has to be porous and permeable to gas and water in addition to having good conductivity to electrons and heat. Graphitized carbon fiber paper and carbon cloth are two commonly used DM materials. The DM fabrication process is described in Reference 10.

DM is usually made to be hydrophobic in order to facilitate water transport through it and to avoid flooding in the presence of liquid water. Because water is produced in the
cathode, a thin (<50μm thick) microporous layer (MPL), is usually placed between the DM and the electrode, assisting water removal from the cathode to the FF. The MPL usually consists of carbon or graphite particles mixed with a polymeric binder, such as polytetrafluoroethylene (PTFE). It is porous and is supposed, as well, to improve the interface contact between the DM and the electrode.

**Flow Field:** The flow field (FF) consists of channels and lands, which deliver reactant to the anode or the cathode, and provides thermal and electronic conduction paths. It also acts as a current collector. The FF is usually made of graphitized carbon or a metal. The pattern of the channels determines the reactant pressure drop between the inlet and outlet of the cell, and subsequently affects the distribution of the reactant and thus the current distribution over the face of the electrode.

1.1.2 Sources of voltage loss

For a H₂/O₂ fuel cell, the theoretical cell voltage at zero current is the reversible cell voltage ($E_{rev}$). In reality, once current is applied, several voltage drops occur. To optimize cell performance and improve durability, it is necessary to identify the voltage losses and to quantify each term. The cell voltage ($E_{cell}$) under load is given by subtracting each loss term from the theoretical cell voltage, as shown in Equation 1.4

$$E_{cell} = E_{rev} - i \cdot HFR - \eta_{HOR} - \eta_{ORR} - i\left(R_{H^+,an}^{\text{eff}} + R_{H^+,cath}^{\text{eff}}\right) - \eta_{tx}$$  \[1.4\]

where $E_{rev}$ is the thermodynamic cell potential determined by the two half cell reactions, HOR at the anode and ORR at the cathode, and is a function of temperature, reactant partial pressures, and water vapor activity\textsuperscript{11, 12}.
\[
E_{\text{rev}} = 1.23 - 0.9 \times 10^{-3} (T - 298) + \frac{2.303RT}{4F} \log \left( \frac{p_{H_2}}{p_{H_2}^*} \right) \left( \frac{p_{O_2}}{p_{O_2}^*} \right) \left( \frac{a_{H_2O}^*}{a_{H_2O}} \right)^2 \]  

[1.5]

Here, \( T \) is the cell temperature in units of K, \( R \) is the universal gas constant (8.314 J⋅mol\(^{-1}\)⋅K\(^{-1}\)), \( F \) is the Faraday constant (96485 C/mol), \( p_{H_2} \) and \( p_{O_2} \) partial pressure of H\(_2\) and O\(_2\), respectively. \( p_{H_2}^* \) and \( p_{O_2}^* \) are the reference pressures of H\(_2\) and O\(_2\), respectively at 101.3 kPa. \( a_{H_2O} \) is water vapor activity and \( a_{H_2O}^* \) is reference water vapor activity (\( a_{H_2O}^* = 1 \)) corresponding to 100%RH at a given temperature. \( a_{H_2O} / a_{H_2O}^* = 1 \) for RH\( \leq 100\% \), and \( a_{H_2O} / a_{H_2O}^* \equiv RH \) (given as a fraction rather than in %) at subsaturated condition.

The HFR term in Equation 1.4 is high frequency resistance in units of \( \Omega \cdot \text{cm}^2 \), including the proton resistance in the membrane and the electronic resistance across the cell, consisting mainly of the contact resistance between cell components, especially between the DM and FF. The proton resistance in the membrane is a function of temperature and relative humidity, while the electronic resistance is considered independent of operating conditions. The HFR can be determined using AC impedance, by reading the intercept of Nyquist plot with real axis in a complex coordinate. The voltage loss caused by HFR follows Ohm’s law and is proportional to the applied current density.

The third and fourth terms in Equation 1.4, \( \eta_{\text{HOR}} \) and \( \eta_{\text{ORR}} \), are kinetics losses resulting from the charge transfer resistances to HOR and ORR on the Pt catalyst, respectively. These two overpotentials have been individually and extensively studied in liquid electrolyte\(^{13-18} \) as well as in PEM fuel cells.\(^{19-26} \) The HOR has a fast kinetics,\(^{13-16} \).
exhibiting an exchange current density ranging from 1mA/cm² to 600mA/cm². The reported low values result from the lack of compensation for mass transport and ohmic resistance, as reported by Neyerlin et al., who demonstrated that the true exchange current densities for the HOR/HER (hydrogen evolution reaction) in a PEMFC is on the order of 200-600mA/cm². This high exchange current density results in <3mV overpotential for a Pt loading of 0.05 mg/cm² at saturated condition. On the other hand, the oxygen reduction reaction (ORR) kinetics is very slow, about 7 orders slower than the HOR reaction, and the overpotential caused by ORR kinetics (η_ORR) in PEM fuel cells has been quantified to be substantial over a wide range of temperatures and oxygen partial pressures. The η_ORR is given by

$$\eta_{\text{ORR}} = \frac{2.303RT}{\alpha c F} \log \left( \frac{i + i_x}{10L_{Pt,\text{cath}} \cdot A_{Pt,el} \cdot i_{o,s}^* \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^7} \right)$$

where $\alpha_c$ is the cathodic transfer coefficient, determined to be 1 based on Neyerlin et al.’s study. $i_x$ is the current produced by permeated H₂ crossover from the anode to the cathode in unit of A/cm², which can be experimentally determined in a H₂ (anode)/N₂ (cathode) cell. $L_{Pt,\text{cath}}$ is the cathode Pt loading in mg/cm² MEA, and $A_{Pt,el}$ is the Pt specific surface area in m²/gPt determined from the H adsorption/desorption charge of cyclic voltammograms. $i_{o,s}^*$ (A/cm²Pt) is the catalyst-specific exchange current density normalized to reference oxygen partial pressure ($p_{O_2}^*$) of 101.3 kPa at the reference
temperature \((T^*)\) of 80°C, and \(\gamma\) is the kinetic reaction order with respect to oxygen partial pressure.

The two items in the parenthesis, \(R_{H^+,an}^{\text{eff}}\) and \(R_{H^+,cath}^{\text{eff}}\), in Equation 1.4 are the effective proton transport resistance in the anode and cathode, respectively. Because of the very fast hydrogen oxidation reaction (HOR) kinetics on platinum catalyst in PEM fuel cells,\(^{21}\) the anode reaction generally occurs very near the interface between the anode catalyst layer and the membrane. Consequently, the pathway of protons released from the reaction site to the membrane is very short, and thus proton resistance in the anode catalyst layer is negligible. However, when drawing large current densities at very low relative humidity and/or at very low temperature during a freeze start-up, this loss could become significant and has to be considered.\(^{30, 31}\) In the cathode, due to the slow kinetics of ORR, the reaction penetrates deeper into the electrode thickness. Therefore, in addition to the overpotential loss of the ORR, the overpotential due to proton resistance could be substantial. The determination of voltage loss induced by this resistance is the main focus of this thesis.

The last voltage loss term in Equation 1.4, \(\eta_{tx}\), is the mass transport loss resulting from the reactant partial pressure difference between the FF and electrode, especially in the cathode due to the slow \(O_2\) diffusion. When pure \(O_2\) is used instead of air, this term is negligible in well prepared electrodes.\(^{32}\) Direct measurement of mass transport overpotential is difficult, therefore pure oxygen and differential operating conditions are employed in order to eliminate \(\eta_{tx}\) and to accurately measure the voltage loss due to proton resistance in the cathode.
1.2 CATHODE ELECTRODE INGREDIENTS

The electrode is composed of carbon supported catalysts and ionomer, respectively providing pathways for electrons and protons. The catalyst is typically Pt or alloyed-Pt with an average size of 2-3 nm dispersed on porous carbon material (30-40 nm in diameter for a single particle), such as the commercially available types: Vulcan XC-72C (amorphous), graphitized Vulcan, Ketjenblack (KB, amorphous) and graphitized KB, which possess good electronic conductivity, high BET surface areas, and high porosity.\textsuperscript{33}

Though usually carbon only accounts for \(~50\%\text{wt.}~\) of the catalyst, due to its much smaller density (~2g/cm\textsuperscript{3}) than Pt metal (~21.5g/cm\textsuperscript{3}), the carbon volume fraction is ca. 10 times larger than that of Pt and the carbon surface area is much larger than the Pt surface area. Therefore, catalyst properties are significantly affected by the properties of the carbon support. Due to their difference in microstructure and crystallinity, the carbon supports exhibit different Pt dispersion and resistance to corrosion. Figure 1.3 demonstrates the Pt distribution on different carbon supports under observation of Z-contrast Scanning Transmission Electron Microscopy (STEM).\textsuperscript{34} The bright areas are dispersed Pt particles with similar size for all types of carbon.
Figure 1.3: Platinum distribution on different carbon supports under Z-contrast STEM. a) amorphous Vulcan, b) amorphous Ketjenblack, c) graphitized Vulcan, and d) graphitized Ketjenblack

Figure 1.3 a and b shows amorphous Vulcan and KB, respectively; c and d are the corresponding graphitized types. It shows that Pt distributes uniformly on both amorphous carbons. However, it prefers the edges of the graphitized carbon probably due to the different surface energy between the basal plane and the edges, resulting in Pt agglomerates along the graphite edges. Consequently, Pt on amorphous carbons exhibit higher available electrochemical area than on graphitized carbons. On the other hand, graphitized carbon is more corrosion resistant. In summary, catalyst selection depends
on its application and represents a balance between its electrochemical area (performance) and corrosion resistance (durability).

Another important component of the electrode is the proton conducting ionomer. It was not until the 1980s that researchers started to incorporate proton conducting ionomer with catalysts to prepare the ink for the electrode. The current procedure for the preparation of the electrodes and the MEA was originally developed by Wilson and Gottesfeld. The ionomer covers the catalyst, and its distribution on the catalyst is determined by the carbon surface properties, such as porosity and hydrophobicity. Furthermore, the ionomer distribution directly affects the electrode utilization.

The benefit of the ionomer network formed within the electrode is reported in the literature, as it allows for proton transport within the electrode, and electrode performance is thus strongly enhanced by the inclusion of ionomer within the electrode. Insufficient ionomer loading in the electrode may lead to significant voltage losses due to increased proton resistance, while too much ionomer in the electrode could block the access of the gaseous reactant to the Pt, generating significant diffusion overpotential. The amount of ionomer is controlled by ionomer-to-carbon weight ratio (I/C-ratio) while making the electrode. Figure 1.4 illustrates the empirical correlation among the volume fractions of catalyst, ionomer, and void as a function of I/C-ratio in typical PEM fuel cell electrode. It shows that for the same amount of carbon, increasing I/C-ratio results in nearly the same increase in the ionomer volume fraction and a decrease in the void volume fraction. Therefore, optimization of the I/C-ratio is critical to the performance of the electrode. Boyer et al. found that the proton conductivity at fully humidified conditions of electrodes composed of carbon-supported Pt catalyst (Pt/C) and Nafion®
ionomer is proportional to the volume fraction of the ionomer ranging from ~10% to ~50% (corresponding to the ionomer/carbon weight ratio (I/C-ratio) of 0.5 to 2.5) in the electrode; however, no measurements were conducted under low-RH conditions which are relevant for automotive applications. The latter will be extensively studied in later Chapters of this thesis.

![Graph](image)

**Figure 1.4**: Volume fractions of catalyst (platinum dispersed on carbon support), \( \varepsilon_C + \varepsilon_{Pt} \), and ionomer, \( \varepsilon_I \), as well as electrode void volumes, \( \varepsilon_{void} \), as a function of I/C ratio (ionomer/carbon weight ratio) of typical PEM fuel cell electrodes.

The voltage loss caused by the proton resistance can be substantial when operating at high current densities at dry condition and/or low temperature. The development of a reliable and experimentally feasible method to measure the proton resistance is highly desirable, as modeling efforts are attempted to predict cell performance. Among
attempts to isolate the electrode proton resistance.\textsuperscript{43-45} AC impedance is considered a powerful tool because of its capability to provide information about the ORR charge transfer, proton resistance and mass transport in the cathode. The main drawback is the difficulty in isolating and measuring electrode proton resistance by AC impedance in an operating cell. Additionally, a viable model of electrode structure is needed. The widely applied model is the thin-film flooded agglomerate model,\textsuperscript{46} which considers the electrode as a structure with agglomerate region consisting of a thin film diffusion element.

Researchers have started to measure electrode proton resistance using AC impedance in a H\textsubscript{2}/N\textsubscript{2} cell, eliminating the effects of ORR kinetics and mass transport resistance.\textsuperscript{43, 47, 48} Meanwhile, important progress has been made recently in modeling the electrode structure and analyzing data obtained by AC impedance.\textsuperscript{43, 47, 49, 50} Nevertheless, a well-established experimental method is still lacking. Several aspects need to be considered while designing the experiment set-up to measure the electrode proton resistance, such as operating conditions (i.e., gas flow rate, distribution of RH and pressure over the cell) and applied potential selection, which determines the Pt surface species. In this thesis, a comprehensive method will be developed to study the electrode proton resistance. The effects of electrode components, such as ionomer and carbon support, on the electrode proton resistance were recently reported.\textsuperscript{38, 48} Iden et al.\textsuperscript{51} studied the effect of carbon support on proton conduction in a pseudo-electrode using carbon without Pt in a H\textsubscript{2} pump cell, however the surface properties of carbon with or without Pt are different. The effects of ionomer EW and catalyst-dispersed carbon supports on the proton resistance in a cathode are investigated in this thesis, by AC impedance.
In addition, the understanding of electrode structure, such as pore size, ionomer distribution, its volume fraction and electrode porosity, is needed in order to evaluate the electronic and proton resistances and reactant transport properties in the electrode. Gu et al.\textsuperscript{30} recently provided a thorough overview on how to obtain these transport properties.

1.3 RESEARCH GOALS

The goal of this thesis is to investigate proton transport in the cathode and to quantify the voltage loss induced by this resistance at various operating conditions. The main goal is to shed light on electrode design and optimization. First of all, a method is developed to measure proton resistance in the electrode and the membrane by using AC impedance in H$_2$/N$_2$ cells, as presented in Chapter 2. The effects of the electrode components (ionomer and catalyst carbon support) on the electrode proton resistance are further investigated. A theoretical method is introduced to determine the local RH in the cathode as a function of RH in the channel and the applied current densities, based on the fundamental water transport in H$_2$/O$_2$. Cell performance is compared with model prediction using the correlation between the proton and the RH determined in Chapter 2. Finally, some preliminary studies on the Pt oxide coverage are conducted in order to further understand the ORR kinetics. The Pt oxide coverage is measured as a function of potential, RH, and exposure history to O$_2$. The detailed goal of each chapter is described in the following section.

\textbf{Chapter 2:} Proton conduction and oxygen reduction kinetics in PEM fuel cell cathodes: effects of the ionomer-to-carbon ratio and relative humidity
Objective: Develop a method to quantify the proton resistance in the cathode, and to investigate the effect of ionomer to carbon weight ratio (I/C-ratio) and RH on the electrode proton resistance and cell performance as well as the effect of RH on the ORR kinetics.

This chapter details how to determine the experimental set-up, namely the selection of applied potential and cathode exposure atmosphere. The obtained data is analyzed by a 1-D transmission-line model. The dependence of the electrode proton resistance on the electrode I/C ratio and RH is investigated at 80°C in H₂/N₂ cells. This method is validated by applying the obtained proton resistance to an operating cell performance model at low current density assuming the RH and temperature gradients are negligible. By comparing the data with the model, the effect of RH on ORR kinetics is discussed.

Chapter 3: Proton conduction in PEM fuel cell cathodes: effects of electrode thickness and ionomer equivalent weight

Objective: Investigate the proton resistivity in electrodes with various thickness and EW ionomers, and compare the dependence of cell performance on ionomer EW.

Proton resistivity in a uniform electrode is tested to be independent of electrode thickness. The proton resistivity and cell performance for electrodes with different EW ionomers but the same catalyst at the same I/C-ratio are also investigated. The proton resistivity in electrode and ionomer cast membranes is compared, and conclusive suggestions in regard to electrode designs are proposed.

Chapter 4: Model for proton conduction in PEM fuel cell cathodes
Objective: Develop a model for proton conduction in PEM fuel cell and relate electrode proton conduction to ionomer properties and its volume fraction and carbon support.

A model is developed to correlate the proton conduction in electrode to the ionomer bulk proton conductivity considering the ionomer swelling behavior due to the water uptake, the porosity and roughness of the Pt-dispersed carbon support.

Chapter 5: Effects of catalyst carbon support on proton conduction and electrode performance in PEM Fuel Cells

Objective: Investigate the proton resistivity and cell performance in electrodes with different catalyst carbon supports, and compare the RH effects on the kinetics of catalysts with different carbon supports.

Based on an understanding of ionomer distribution on carbon supports with different BET areas, higher surface area indicates higher electrode proton resistivity. The proton resistivities are compared between electrodes with Pt/Vulcan and Pt/Ketjenblack supports with the same ionomer and I/C-ratio is applied. Their performance in H₂/O₂ cells is also compared and discussed.

Chapter 6: Determination of local electrode relative humidity (RH) in a H₂/O₂ cell

Objective: Develop a 1-D model for water transport in order to predict the local RH in the membrane and the cathode, and validate the model by comparing experimental data with the predicted data.

The proton resistance in the membrane and the cathode is predicted based on the RH distribution predicted by the 1-D model. The sensitivity of transport properties used in the
model is discussed and tested. The experimentally determined proton resistance in the cathode is compared with the model’s prediction.

**Chapter 7: Measurements of platinum oxide coverage in a PEM fuel cell**

Objective: Study the effects of temperature, RH and the history of past exposure to O₂-containing atmosphere on Pt oxide formation on dispersed Pt and provide information on how to improve ORR kinetics.

The charge involved to form the oxide on the Pt is measured using cyclic voltammogram at various temperatures, potentials, history of exposure to various O₂ concentrations (0-100%) and exposure time.

**REFERENCES**


Chapter 2
Proton Conduction and Oxygen Reduction Kinetics in PEM Fuel Cell Cathodes: Effects of Ionomer-to-Carbon Ratio and Relative Humidity

2.1 INTRODUCTION

Proton exchange membrane (PEM) fuel cells are able to achieve much higher fuel efficiency than internal combustion engines by transforming chemical energy to electricity. However, in reality, several resistances can cause inefficiency or voltage losses during fuel cell operation: kinetic losses due to the slow electrochemical reaction rate, ohmic losses caused by proton transport in the ionomer electrolyte in the membrane and in the catalyst layers, electronic resistance mainly due to contact resistance between the diffusion media (DM) and the flow-field, and slow mass transport of reactants. The catalyst layer is composed of carbon-supported platinum catalyst and a proton-conducting ionomer. Even though the voltage loss due to the cathode kinetics is the dominant loss in the fuel cell, the losses due to proton transport in the electrodes can be substantial depending on their ionomer content and the operating conditions, so that it is of great importance to quantify these losses as a function of electrode composition and relative humidity (RH) in order to optimize electrodes.\textsuperscript{1,2}

Because of the very fast hydrogen oxidation reaction (HOR) kinetics on platinum catalysts in PEMFCs,\textsuperscript{3} the anode reaction generally occurs very near the interface between the anode catalyst layer and the membrane. Consequently, the pathway of proton released from the reaction site to the membrane is very short, and thus in the anode
catalyst layer the effective proton resistance is negligible. However, when drawing large
current densities at very low relative humidity and/or at very low temperature during a
freeze start-up, this loss could become significant and has to be determined.\textsuperscript{4, 5}
Nevertheless, for the experimental conditions in this study, the protonic resistance in the
anode will be shown to be negligible, resulting in a maximum voltage loss of \( \sim 1.5 \text{ mV}, \)
and will thus be ignored.\textsuperscript{5}

On the other hand, the oxygen reduction reaction (ORR) kinetics are very slow,\textsuperscript{6-9}
and the overpotential caused by ORR kinetics in PEMFCs has been quantified over a
wide range of temperatures and oxygen partial pressures.\textsuperscript{10, 11} Since the ORR is a three
phase heterogeneous reaction, the \( \text{O}_2 \) in the gas phase, electrons in the solid phase, and
protons in the ionomer phase need to intimately coexist at the reaction sites of the
platinum catalyst. The transport of each species to or away from the reaction site could be
a limiting step, depending on the proton resistance in the electrode, in addition to the
slow kinetics of the ORR reaction. The benefit of the ionomer network formed within the
electrode is reported in the literature,\textsuperscript{12, 13} as it allows for proton transport within the
electrodes, and electrode performance is thus strongly enhanced by the addition of
ionomer in the electrodes.\textsuperscript{14} Insufficient ionomer loadings in the electrode may lead to
significant voltage losses due to increased proton resistance. Boyer \textit{et al.}\textsuperscript{15} found that the
proton conductivity at fully humidified conditions of electrodes composed of carbon-
supported Pt catalyst (Pt/C) and Nafion\textsuperscript{©} ionomer is proportional to the volume fraction
of the ionomer ranging from \( \sim 10\% \) to \( \sim 50\% \) (corresponding to the ionomer/carbon
weight ratio (I/C-ratio) of 0.5/1 to 2.5/1\textsuperscript{15}) in the electrode; however, no measurements
were conducted under low-RH conditions which are relevant for automotive applications.
In general, the resistance to the proton conduction through the entire thickness of the electrode (in $\Omega \cdot \text{cm}^2$), $R_{H^+,\text{cath}}$, strongly increases with decreasing relative humidity and only slightly decreases with increasing temperature. High $R_{H^+,\text{cath}}$ values result in an inhomogeneous current distribution in the cathode, lowering the cathode catalyst utilization, and producing a voltage loss which can be calculated by using an effective proton resistance in the cathode, $R_{H^+,\text{cath}}^{\text{eff}}$ (different from $R_{H^+,\text{cath}}$), as was shown in Ref. 16. Depending on the ionomer content of the cathode electrode, the induced voltage losses can become significant under low RH conditions and during freeze start-up.\textsuperscript{4, 5} To date, no systematically measured $R_{H^+,\text{cath}}$ data for well-defined electrodes are available in the literature, though several publications have discussed the determination of $R_{H^+,\text{cath}}$ by both mathematical models and experimental methods.\textsuperscript{17-21}

2.2 METHOD DEVELOPMENT

It has been shown\textsuperscript{17-19} that the AC impedance response of the electrode in a PEMFC can be described by a one dimensional transmission-line model, consisting of a series of differential electrode thickness elements exhibiting protonic resistance, double layer capacitance and charge transfer resistance, shown in Figure 2.1a. In this model, the through-plane proton resistance of the membrane ($R_{\text{mem}}$), and the electronic resistances across the flow field and diffusion media to the electrode ($R_{\text{DM/FF}}$) are purely Ohmic, meaning that the potential drop across these resistors is directly proportional to the current. On the other hand, the charge-transfer resistances of the electrochemical reactions in the electrode ($R_{\text{ct,i}}$) are non-linear for the $O_2$ reduction reaction (i.e.,
following Tafel-kinetics, where the potential drop is proportional to the logarithm of the current) and are in parallel to the potential- and RH-dependent catalyst capacitances ($C_i$).

Though the frequency response of an operating membrane electrode assembly (MEA) can be modeled using the transmission line approach shown in Figure 2.1a, extraction of meaningful physical-chemical parameters is complicated by the non-linearity of the charge-transfer resistances and the dependence of the capacitive terms on potential and RH.$^{1,22}$

A less complex model can be obtained by using a H$_2$-fed anode (reference/counter electrode) and a N$_2$-purged cathode (working electrode), in which case the non-linear charge-transfer resistances vanish (i.e., $R_{ct,i}$ elements in Figure 2.1a disappear). This simplification does not impact any of the transmission line model elements for which a measurement is sought ($R_{mem}$, $R_{H2^{+}}$, $R_{cath,i}$, and $C_i$) shown in Figure 2.1b. It should be noted that the use of a H$_2$-fed counter/reference electrode allows precise determination of the potential of the N$_2$-fed working electrode, which allows a precise determination of the electrode capacitance (see discussion below). If both electrodes were fed with inert gas, the absolute potential of the working electrode would be unknown and possibly shifting during the experiment (unless an independent reference electrode is used), which would make it difficult, if not impossible, to quantify the AC impedance results.
Figure 2.1: MEA transmission-line model, showing the protonic membrane resistance ($R_{\text{mem}}$) and incremental electrode proton resistances ($R_{H^+, \text{cath}, i}$) as well as the electronic resistance ($R_{\text{electronic}}$) which originates mainly from the DM/FF contact resistance ($R_{\text{DM/FF}}$). These Ohmic resistances are connected by (a): the incremental potential-dependent catalyst capacitances ($C_i$) in parallel to non-linear charge-transfer resistances ($R_{ct,i}$) in $H_2/O_2$ and (b): the incremental potential-dependent catalyst capacitances ($C_i$) only in $H_2/N_2$. 
Figure 2.2: Cyclic voltammograms of \( \approx 50\% \) Pt/Vulcan at 80\(^\circ\)C and 20 mV/s at various RH-levels with H\(_2\)/N\(_2\) (2000/50 sccm) feeds at the counter/working electrode at ambient pressure. Current densities were divided by the voltage scan rate to obtain the capacitive response in mF/cm\(^2\)_MEA. Pt-loading=0.40mgPt/cm\(^2\), \( A_{Pt,el}=46\text{m}^2/\text{gPt} \), electrode I/C=0.58. The dashed line gives the potential (0.186V vs RHE, 100kPa\( \text{H}_2 \) at 80\(^\circ\)C, which will convert to 0.2V vs RHE at 80\(^\circ\)C, 253kPa\( \text{H}_2 \)) applied for the impedance measurement. The short dash dotted line shows dependence of the HOR/HER current density measured at 80\(^\circ\)C, 122\%RH with H\(_2\)/N\(_2\) (2000/2000 sccm, \( p_{\text{H}_2}=p_{\text{N}_2}=253\text{kPa} \)) on the potential, which has been converted to the RHE at 80\(^\circ\)C, 100kPa\( \text{H}_2 \).

Another simplification relates to the RH-dependence of the capacitive elements (\( C_i \)), which becomes negligible when AC impedance evaluation is conducted at a potential which is within the H-adsorption/desorption (HAD) region (\( \approx 0.05-0.25 \) V). This can be shown by the cyclic voltammograms (CV) of a typical Pt-catalyst (\( \approx 50\% \) Pt/Vulcan) at different RH conditions (see Figure 2.2) obtained with the same experimental set-up as in Ref. 22, where the capacitance is obtained by dividing the
current by the voltage sweep rate. Quite clearly, the electrode capacitance depends on RH in most of the potential region, but is nearly independent of RH in the HAD region, suggesting that the formation/desorption of adsorbed oxygen-containing species (OH\textsubscript{ad}) depends on water activity, while that of adsorbed H does not. In addition, owing to the fast H-adsorption/desorption kinetics, the potential-dependent capacitive current in this region are rather insensitive to the voltage sweep rate (up to \(\approx 10\) V/s based on the literature\textsuperscript{23}). Thus, at the voltage perturbation of 1 mV (amplitude) used in our study, the H-adsorption/desorption pseudo capacitance is expected to be constant up to a frequency of \(\approx 10\) kHz. Therefore, for the H\textsubscript{2}/N\textsubscript{2} AC impedance measurements in the HAD region the cathode capacity can be considered RH- and frequency-independent (up to 10 kHz).

One additional advantage for conducting AC impedance measurements in the HAD region is related to the fact that the 5 to 10-fold higher electrode capacity in this region, compared to the double-layer region (0.35-0.55 V, see Figure 2.2), allows for evaluation of the electrode proton resistance at lower frequencies, where interferences from commonly observed inductive elements are minimized and where electrode capacitance (\(C\text{\textsubscript{cath}}\)) values are frequency independent.

Another important criterion that must be considered when conducting AC impedance measurements in H\textsubscript{2}/N\textsubscript{2} in the HAD-region is that the chosen potential should be sufficiently positive so that the crossover H\textsubscript{2} oxidation is permeation-limited, i.e., independent of potential. For the chosen operating conditions (80\degree\textordmasculineC, and 253kPa H\textsubscript{2} partial pressure at all RHs) and the H\textsubscript{2} permeation rate of a typical 25 \(\mu\)m perfluorosulfonic acid (PFSA) membrane this requirement is satisfied at \(>0.15\) V vs. the reversible hydrogen electrode (RHE), where the oxidation of H\textsubscript{2} permeating through the
membrane becomes diffusion limited (see dot-dashed line in Figure 2.2). Thus, at the chosen potential of 0.2 V for the AC impedance measurements, the H₂ crossover currents will not influence the AC impedance signal.

In summary, if AC impedance measurements are conducted using a H₂/N₂ flow configuration, i.e., with a N₂-fed working electrode and a H₂-fed reference/counter electrode at a potential of +0.2 V vs. a H₂-fed anode, the transmission line model can be significantly simplified and the capacitances (Cᵢ) are reasonably independent of RH and frequency, allowing for the most precise quantification of the RH-dependent membrane (Rₘₑₘ) and electrode (R⁺ₜ,cat) resistances. In this case, hydrogen evolution will occur at the H₂-fed counter/reference electrode and the oxidation of the H₂ permeating through the membrane will occur at the N₂-fed working electrode. The DC current thus corresponds to the limiting current for the hydrogen crossover and this current occurs at the cathode/membrane interface, leaving the entire catalyst layer without Faradaic resistance, which greatly simplifies the analysis. The AC impedance response of the working electrode can be described by a simple transmission-line model of capacitors (Cᵢ) in parallel to the electrode’s proton resistances (R⁺ₜ,cat,i), as was recently analyzed.¹⁷,¹⁹

It is known that R⁺ₜ,cat has significant impact on the performance of a H₂/O₂ cell.¹⁶ In this study, we developed a method to quantify the variation of R⁺ₜ,cat as a function of both an electrode’s ionomer/carbon weight ratio (I/C-ratio) and the relative humidity to which an electrode is exposed. In what follows, we first describe AC impedance experiments to measure both membrane resistance and the cathode proton resistance in an H₂/N₂ cell configuration. Then we use the thus established RH-dependent R⁺ₜ,cat values for a given electrode together with the measured membrane resistance to evaluate the true
resistance corrected cell voltage, $E_{IR-free}$, of an H$_2$/O$_2$ cell. This resistance correction includes both the conventionally used high-frequency resistance (HFR) term, correcting for membrane and contact resistances, as well as the ohmic losses within the cathode due to the resistance to the electrode proton conduction. By this approach we seek to validate that electrode proton resistivity, $\rho_{H^+,cath}$ (ratio of $R_{H^+,cath}$ over cathode thickness, which is $28 \pm 2\mu$m/(mg$_C$/cm$^2$) for I/C of $<3/1$) is indeed an intrinsic electrode property which determines its performance. Finally, we conclude with findings that will provide guidelines for electrode design and fabrication, and shed light on cell performance prediction. It should be noted that the assumption of uniform ionomer distribution in these model electrodes is supported by the analysis.

2.3 EXPERIMENTAL

Membrane Electrode Assembly (MEA) Components and Fabrication

MEAs with 50 cm$^2$ active area were fabricated in-house by hot pressing electrode decals onto a 25 µm thick Nafion-211® membranes (DuPont, USA) with 1050 equivalent weight (EW), so that the ionomer used in the electrodes had the same EW as the membrane. Anode Pt loadings were ~0.4 mg$_{pt}$/cm$^2$ and all anodes had an Ionomer/Carbon (I/C) weight ratio of ~0.9/1. The I/C-ratios of the different cathodes ranged from 0.29/1 to 1.15/1, using a ~50% Pt/Vulcan catalyst (Tanaka, Japan) at a nominal loading of ~0.4 mg$_{pt}$/cm$^2$, whereby the precise Pt loading was determined by weight measurements of the decal before and after lamination of the electrode. The thickness of electrodes based on Vulcan or Ketjenblack supports and for I/C-ratios of <3 only depends on the carbon loading of the electrode, so that the electrode thickness can be calculated from
the carbon loading multiplied by $28 \text{ \mu m} / (\text{mgC/cm}^2_{\text{electrode}})$. The I/C-ratios, Pt surface areas, Pt loadings, and thicknesses of all the cathodes studied here are shown in Table 2.1.

Table 2.1: Electrode properties of cathodes produced from 50% Pt/Vulcan catalyst (Tanaka, Japan) and DE2021® ionomer (DuPont, USA): cathode ionomer to carbon weight ratio, I/C-ratio, in-situ measured Pt surface area, $A_{Pt,el}$, Pt loading, $L_{ca}$, and cathode thickness, $t_{cath}$. Using the data at 122% RH, specific activities, $i^s_{x}(0.9V)$, and mass activities, $i^m_{x}(0.9V)$, at 0.9 V as well as exchange current densities, $i^*_{o,s}$, were obtained by using Eqs. 5 and 11 from Reference 10 and are normalized to reference conditions of $T^*=80^\circ\text{C}$ and $p_{H_2}^*=p_{O_2}^* = 101.3 \text{ kPa}_{abs}$.

<table>
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<th>I/C-ratio</th>
<th>$A_{Pt,el}$ [m$^2$/g$_{Pt}$]</th>
<th>$L_{ca}$ [mg$_{Pt}$/cm$^2$]</th>
<th>$t_{cath}$ [\mu m]</th>
<th>$i^s_{x}(0.9V)$ [A/cm$^2_{Pt}$]</th>
<th>$i^m_{x}(0.9V)$ [A/mg$_{Pt}$]</th>
<th>$i^*<em>{o,s}$ [A/cm$^2</em>{Pt}$]</th>
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<td>13.3</td>
<td>1.6E-04</td>
<td>0.071</td>
<td>1.6E-08</td>
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<td>0.078</td>
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AC Impedance Measurements

AC impedance spectra were acquired with a Zahner iM6e (Zahner Inc. Germany). In H$_2$/N$_2$ experiments the N$_2$-fed working electrode ("cathode") was potentiostated at +0.2 V vs. the H$_2$-fed counter/reference electrode ("anode"), with a voltage perturbation of 1 mV (amplitude) at frequencies ranging from 0.5 to 20,000 Hz. Five spectra were collected at each condition to verify reproducibility, with an acquisition time of ~12 minutes per
spectrum and 20 points per decade of frequency. In the case of H₂/O₂ experiments, the current density was maintained at 0.1 A/cm² and H₂ and O₂ partial pressures at each RH-level were maintained at 253 kPa abs (at the cell outlet) by varying the total cell pressure: 300 kPa abs at 122%RH, 287 kPa abs at 75% RH, 276 kPa abs at 50% RH, and 269 kPa abs at 35% RH. H₂ flow rates were held constant at 2100 sccm (standard cubic centimeter per minute), while O₂ and N₂ flow rates were held constant at 1750 sccm. All of the experiments were conducted at 80°C at four different inlet/outlet RH-values under these differential flow conditions, with maximum changes in RH from inlet to outlet of <4 %RH-points (in addition, H₂ and O₂ partial pressure changes were negligible).

It is worth of being mentioned that the usage of high flow rate, high pressure and well controlled humidification is key to obtain clean and reliable impedance spectra, especially at dry conditions. Difficulties were encountered in the initial attempts to obtain AC impedance spectra at low RH under low flow rate (i.e, 50sccm) and ambient pressure. As shown in Figure 2.3a, these operating conditions resulted in very irreproducible impedance spectra most possibly due to the inconsistent humidification control by the test stands at low RH, low flow rates, and ambient pressure due to water condensation in the gas delivery lines. When the flow rate was increased to 2.1/1.75 slpm on the anode and cathode in H₂/N₂ respectively under much higher pressure, the obtained impedance spectra were very reproducible and consistent, as shown in Figure 2.3b. Therefore, all experiments in this work were conducted under high flow rate and high pressures.
Figure 2.3: Five subsequent AC impedance spectra in H₂/N₂ at 50%RH and 80°C using constant flow rate of (a): 50/50 sccm on anode and cathode respectively at ambient pressure (outlet) for MEA with 50%PtCoCr/NEG catalyst at I/C=0.4 and (b): 2.1/1.75 slpm on anode and cathode respectively at 276 kPaabs (outlet) for MEAs with 50% Pt/Vulcan at I/C=0.5.

2.4 RESULTS AND DISCUSSION

2.4.1 \( R_{\text{mem}}, C_{\text{cath}}, \) and \( R_{H^+,\text{cath}} \) in H₂/N₂.

AC impedance data in H₂/N₂ were analyzed by fitting \( R_{H^+,\text{cath}}, C_{\text{cath}} \) and \( HFR \) to a transmission-line model.\(^{19}\) The \( HFR \) is the sum of the RH-dependent proton transport
resistance of the membrane and the cell’s resistances to electron transport, $R_{\text{electronic}}$, which is largely due to the compression dependent contact resistance, $R_{\text{DM/FF}}$, between the flow-field and the diffusion media.\textsuperscript{16, 24} Figure 2.4 compares the Nyquist plot of the experimental AC impedance data (open diamonds in Figure 2.4) obtained in H$_2$/N$_2$ at 75%RH (80°C) with the AC impedance model, showing excellent agreement in the high frequency region (i.e., at low imaginary values, $Im(Z)$) and following the predicted 45° line at lower frequencies as is predicted by the transmission line model.

![Figure 2.4: Comparison of data obtained in H$_2$/N$_2$ at 0.2 V (75%RH, 80°C) with the transmission line model. The open diamonds are the imaginary vs. real parts of the impedance, and the black squares are the imaginary impedance vs. the logarithm of the frequency. Cathode I/C-ratio=0.39/1, Pt-loading= 0.4mg Pt/cm$^2$ with 50%Pt/V (Tanaka, Japan) and DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).](image)
To show the correspondence of frequency to points on the Nyquist plot, the imaginary values are plotted as a function of frequency (shown on the upper horizontal axis) (black squares in Figure 2.4). One sees that the agreement between model and data is almost perfect down to the frequency of ~5Hz. The low frequency data (i.e., toward higher imaginary values $Im(Z)$) deviate slightly from the vertical, purely capacitive line predicted by the model; however, as will be shown later, it still yields a good prediction of electrode capacitance.

The $HFR$-value, i.e., the sum of membrane and contact resistance plus electron bulk resistance (which is negligible), is obtained by extrapolating the high frequency end to its real axis intercept (see Figure 2.4). For a 50 cm$^2$ cell used in this study, the typical value of $R_{DM/FF}$ is ~25 mΩ·cm$^2$ which is obtained by resistance measurements on a fuel cell without MEA (for experimental details see Ref. 10). $R_{mem}$ is obtained by subtracting $R_{DM/FF}$ from the $HFR$-value:

$$R_{mem} = HFR - R_{DM/FF}$$

Figure 2.5 shows the dependence of membrane resistivity, $\rho_{mem}$ (ratio of $R_{mem}$ to RH-dependent membrane thickness), on cathode I/C-ratios. In our previous report,$^1$ a nominal membrane thickness of 25μm was used at all conditions when calculating the $\rho_{mem}$, which is reasonable at subsaturated conditions. However, an error was introduced at 122%RH due to the water uptake of the membrane which results in a significant increase in membrane thickness, as will be calculated below (Membrane expansion due to water absorption is unrestricted, but only occurs in the through-plane direction, since the in-plane expansion is restricted by the diffusion media.). In this report, the membrane
expansion/contraction in the thickness direction is considered at all RH levels, and the corresponding membrane thickness changes with RH and temperature is accounted for when calculating membrane resistivity and later on electrode tortuosity. The water uptake of the membrane is described by Equation 2.2, giving the number of water molecules per proton (also referred to as $\lambda$-value) as a function of RH (note that in Equation 2.2 RH is defined as fraction rather than percentage, valid within RH=0.1 (10%) to RH=0.8 (80%); the temperature $T$ is given in unit of °C and is valid between 30 to 95°C).\textsuperscript{25}

$$
\lambda(RH) = \left[1 + RH^2 \cdot 0.2352 \cdot \left(\frac{T - 30}{30}\right)\right] \cdot \left(14.22 \cdot RH^3 - 18.92 \cdot RH^2 + 13.41 \cdot RH\right) \quad [2.2]
$$

Based on the above equation, the $\lambda$-values at 80°C are 6.6 at 75%RH, 4.1 at 50%RH, and 3.1 at 35%RH, respectively. At 122%RH, i.e., in the presence of liquid water, the $\lambda$-value increases to 22.\textsuperscript{25} As noted above, the volume expansion occurs only in the through-plane direction, and the percentage of membrane thickness variation over its dry thickness, $\Delta t_{mem}/t_{mem,dry}$, is equivalent to the percentage of volume changes ($\Delta V_{mem}/V_{mem,dry}$) as shown in Equation 2.3,\textsuperscript{26,27} which is consistent with the water uptake results.\textsuperscript{26}

$$
\frac{\Delta t_{mem}}{t_{mem,dry}} \equiv \frac{\Delta V_{mem}}{V_{mem,dry}} = \frac{M_w \cdot d_{mem,dry} \cdot \lambda(T,RH)}{d_w \cdot EW} \quad [2.3]
$$

therefore the final membrane thickness can be calculated by

$$
t_{mem(RH,T)} = t_{mem,dry} \left(1 + \frac{M_w \cdot d_{mem,dry} \cdot \lambda(T,RH)}{d_w \cdot EW}\right) \quad [2.4]
$$
where $M_w$ is the water molecular weight (18 g/mol), $d_{\text{mem,dry}}$ is the dry membrane density ($\approx 2 \text{g/cm}^3$ for perfluorosulfonic ionomers like Nafion®)\textsuperscript{28}, $d_w$ is the density of water at 80°C (0.97 g/cm$^3$), EW is the equivalent weight of polymer per mol proton in the unit of g$_{\text{polymer}}$/molH$^+$. Based on the nominal membrane thickness of 25 µm at 25°C and 50% RH ($\lambda = 3.7$, $d_w = 1.00 \text{g/cm}^3$ at 25°C\textsuperscript{29}), the dry membrane thickness is 22 µm. Therefore, the calculated membrane thicknesses are $\approx 39$ µm at 122% RH, $\approx 27$ µm at 75% RH, $\approx 25$ µm at 50% RH, and $\approx 25$ µm at 35% RH, respectively. From these values it is obvious that correction of the nominal membrane thickness to calculate membrane resistivity values is only important when operating in the presence of liquid water (i.e., 122% RH in our case), where actual and nominal thickness values differ by a factor of 1.5.

In principle, the membrane resistivity should increase with decreasing RH but should be independent of the electrode I/C-ratios. The latter is indeed observed for all I/C-ratios at 75% and 122% RH shown in Figure 2.5. However, at the lower RH values, this independence of membrane resistivity from the I/C-ratios is only satisfied for I/C $\geq 0.6/1$. The largest deviation is seen at the lowest RH value of 35% RH and an I/C-ratio of 0.29/1, where the HFR value by extrapolation of the 45°-line is about 0.16 Ω·cm$^2$ ($\rho_{\text{mem}}$ is $\approx 65$ Ω·cm, see Figure 2.5), while the expected value is about 0.23 Ω·cm$^2$ ($\rho_{\text{mem}}$ is $\approx 90$ Ω·cm). At this condition, as will be shown later, the $R_{H^+,\text{cath}}$ -value is 40.4 Ω·cm$^2$ and thus more than two orders of magnitude larger than $R_{\text{mem}}$. In view of the more than 100-fold larger $R_{H^+,\text{cath}}$ value, it is clear that even the slightest deviation from the ideal cathode transmission model would have to lead to significant errors in the experimentally determined membrane resistance. As a consequence, precise membrane resistivities can only be obtained with reasonably conductive cathodes, i.e., at I/C-ratios of $\geq 0.6/1$. 


Figure 2.5: Dependence of membrane resistivity on cathode I/C-ratios at 35%, 50%, 75% and 122% RH in H₂/N₂ at 0.2 V and 80°C. Data points represent independent measurement on different MEAs. 50%Pt/V (Tanaka, Japan) at 0.4mg Pt/cm² with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).

To quantify $R_{H^+,cath}$, it is most straightforward to first determine the cathode capacitance, $C_{cath}$, even though it is in principle possible to extract $R_{H^+,cath}$ without determination of $C_{cath}$ by a curve-fitting procedure outlined in Ref. 5. In a general case as shown in Figure 2.1a, the formula for the impedance is given as Equation 14 in Ref. 18 or Equation 4 in Ref. 19. For the special case with N₂ flowing in the working electrode (see Figure 2.1b), the formula can be simplified

$$Z(f) = \sqrt{\frac{R_{H^+,cath}}{2 \cdot \pi \cdot j \cdot C_{cath} \cdot f}} \coth\left(\sqrt{2 \cdot \pi \cdot j \cdot R_{H^+,cath} \cdot C_{cath} \cdot f}\right) + HFR \quad [2.5]$$

When the frequency, $f$, approaches zero, an approximation to the above formula gives

$$\lim_{f \to 0} Z(f) = \lim_{f \to 0} (\text{Re}(Z) + j \cdot \text{Im}(Z)) \approx \frac{R_{H^+,\text{cath}}}{3} + j \cdot \frac{-1}{2 \cdot \pi \cdot f \cdot C_{\text{cath}}}$$  \[2.6\]

From Equation 2.6, one obtains:

$$C_{\text{cath}} = \lim_{f \to 0} \left[ \frac{-1}{2 \cdot \pi \cdot f \cdot \text{Im}(Z)} \right]$$  \[2.7\]

The term inside the square brackets in Equation 2.7 is plotted as a function of frequency for a series of different cathodes in Figure 2.6, measured at 80°C at 122% RH. As the frequency approaches 1 Hz, the plotted y-value reaches a plateau, which corresponds to the value of $C_{\text{cath}}$.

Figure 2.6: Cathode capacitance for cathodes with various I/C-ratios vs. frequency at 122% RH in H₂/N₂ at 0.2 V and 80°C. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm² with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).
While the capacitance values (125 - 140 mF/cm\(^2\)\(_{\text{MEA}}\)) obtained for the different electrodes in Figure 2.6 are similar, some scatter is observed which is related to small variations in electrode Pt loadings (see Table 2.1) since this capacitance is dominated by the potential-dependent pseudo-capacitance of platinum while the capacitance derived from the carbon support is only a minor contribution (ca. 10%). Therefore, the Pt-specific capacitance reflects a more intrinsic Pt catalyst property and should be independent of I/C-ratio and electrode Pt loading. Therefore, we determined the Pt-specific capacitance according to Equation 2.8

\[
C_{\text{specific}} = \frac{C_{\text{cath}}}{L_{\text{Pt,cath}} \cdot A_{\text{Pt,el}} \cdot 10}
\]  

where \(C_{\text{cath}}\) is in unit of mF/cm\(^2\)\(_{\text{MEA}}\), \(L_{\text{Pt,cath}}\) is the cathode Pt loading in mg Pt/cm\(^2\)\(_{\text{MEA}}\), \(A_{\text{Pt,el}}\) is the Pt specific surface area in m\(^2\)/gPt determined from the H adsorption/desorption charge of cyclic voltammograms, and the factor 10 is a unit conversion factor so that \(C_{\text{specific}}\) is in unit of mF/cm\(^2\)\(_{\text{Pt}}\). Figure 2.7 shows that the \(C_{\text{specific}}\) values for all the MEAs listed in Table 2.1 are indeed nearly independent of the I/C-ratio, with an 11% difference from the lowest to the largest I/C-ratio, which is quite negligible and may be due to the fact that the lower frequency limit of 0.5 Hz was not sufficient to reach the capacitance plateau for very resistive electrodes (i.e., those at low I/C). Overall, the specific capacity of the 50% Pt/Vulcan catalyst is \(\approx 0.77\) mF/cm\(^2\)\(_{\text{Pt}}\) with a standard deviation of 0.05 mF/cm\(^2\)\(_{\text{Pt}}\), suggesting that the measured capacity indeed is an intrinsic electrode property. This value should be comparable to the result from cyclic voltammograms as shown in Figure 2.2, whereby the difference in hydrogen partial pressures between the impedance measurements at 0.2 V (\(p_{\text{H}_2}=253\) kPa\(_{\text{abs}}\)) and the voltammograms in Figure 2.2
\( p_{H_2} = 100 \text{ kPa}_\text{abs} \) signifies that 0.200 V in the impedance experiments corresponds to 0.186V in the voltammograms. At the latter potential, \( C_{\text{cath}} \) is about 165 mF/cm\(^2\) MEA, corresponding to \( C_{\text{specific}} \) of \( \approx 0.89 \) mF/cm\(^2\) Pt. While this is about 15\% higher than the value derived from the AC impedance data, it is smaller than the scatter in values obtained from the AC impedance (see Figure 2.7), supporting the validity of the proposed evaluation of the capacitance using Equation 2.7.

![Figure 2.7](image)

**Figure 2.7:** Specific catalyst capacitance, \( C_{\text{specific}} \), of cathodes with various I/C-ratios at 80°C and 122% RH in H\(_2\)/N\(_2\). Each data point represents an independent measurement on a different MEA. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm\(^2\) with DE2021\(^\circledR\) ionomer (DuPont, USA), NRE211\(^\circledR\) membrane (DuPont, USA).
In the high frequency region, a 45°-line segment appears in the Nyquist plot (see, i.e., Figure 2.4), which can be interpreted by Equation 2.9 (same as Equation 6 in Ref. 19) derived from Equation 2.5

\[
Z(f) \approx \sqrt{\frac{R_{H^+,cath}}{2 \cdot \pi \cdot j \cdot C_{cath} \cdot f}} + HFR \tag{2.9}
\]

which gives

\[
\frac{R_{H^+,cath}}{C_{cath}} = \left[ \text{Im}(Z) \right]^2 \cdot 4 \cdot \pi \cdot f \equiv \left[ \text{Re}(Z) - HFR \right]^2 \cdot 4 \cdot \pi \cdot f \tag{2.10}
\]

where \( f \) is the frequency in Hz and \( C_{cath} \) is the electrode capacitance in F/cm\(^2\)\(_{\text{MEA}}\), if the Nyquist plot axes are given in terms of \( \Omega \cdot \text{cm}^2\)\(_{\text{MEA}}\). Using Equation 2.10 and the above outlined method to determine \( C_{cath} \) values, \( R_{H^+,cath} \) was obtained for different cathode I/C-ratios and RH-levels, using all the MEAs shown in Table 2.1. To obtain a more intrinsic electrode structural parameter, \( R_{H^+,cath} \) was converted into \( \rho_{H^+,cath} \) by dividing \( R_{H^+,cath} \) by the cathode thickness, which is 28 ± 2\( \mu \)m/(mgC/cm\(^2\)) for I/C of <3/1.\(^5\) Figure 2.8 illustrates the strong dependence of \( \rho_{H^+,cath} \) on cathode I/C-ratio at 75%, 50%, and 35% RH, increasing by a factor of 50 to 100 as the I/C-ratio decreases from 1.15/1 to 0.29/1. At 122% RH, \( R_{H^+,cath} \) could only be determined for electrodes with lower I/C-ratios, since at I/C>0.8 the electrode resistance was too small to be measured within reasonable precision; thus Figure 2.8 only shows \( \rho_{H^+,cath} \) up to I/C=0.8. Comparing Figures 2.5 and 2.8, it becomes clear that the electrode resistivities are 10 to 100-fold larger at low I/C-
ratios so that one might expect significant proton conduction losses in these electrodes compared to ohmic losses in the membrane.

Figure 2.8: Dependence of cathode proton resistivities on I/C-ratios at 35%, 50%, and 75% RH in H₂/N₂ at 80°C. Data points represent independent measurement on different MEAs. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm² with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).

To get a better understanding of the impact of I/C-ratio on electrode proton resistivity, it can be formulated more generally as:

\[
\rho_{H^+,cath} = \frac{R_{H^+,cath}}{t_{cath}} = \frac{1}{\kappa_{(T, RH)} \cdot \varepsilon_i / \tau_{(\varepsilon_i)}}
\]  

[2.11]
where \( \kappa(T, \text{RH}) \) is the temperature- and RH-dependent ionomer conductivity, \( \varepsilon_i \) is the ionomer volume fraction in the electrode which can be evaluated by Equation 2.12, which is the same as Equation A.5 (see the detailed derivation in the Appendix A), and \( \tau(\varepsilon_i) \) is the tortuosity which in the most general case may depend on \( \varepsilon_i \).

\[
\varepsilon_i = \left( \frac{I}{C} \right) \frac{10}{f_t \cdot d_{t,\text{dry}}} \left( 1 + \frac{M_w \cdot d_{t,\text{dry}} \cdot \lambda}{d_w \cdot EW} \right) \tag{2.12}
\]

where \( I/C \) is the weight ratio of ionomer to carbon in the electrode, \( f_t \) is 28 ± 2\( \mu \)m/(mgC/cm\(^2\)) for I/C of <3, \( d_{t,\text{dry}} \) is the density of dry ionomer equivalent to \( d_{\text{mem, dry}} \) as defined previously in the text, which is 2g/cm\(^3\), \( d_w \) is the density of water (equal to 0.97g/cm\(^3\) at 80°C), \( M_w \) is water molar molecular weight (g/mol), the values of \( \lambda \) is calculated from Equation 2.2, and \( EW \) is the equivalent weight of the ionomer in the electrode, which is 1050 g/mol\( \text{H}^+ \).

If the same ionomer is used in the membrane and the electrode as in the present work, Equation 2.11 may be rewritten to obtain the effective tortuosity in the electrode:

\[
\tau(\varepsilon_i) = \frac{\rho_{\text{H}^+ , \text{mem}} \cdot \varepsilon_i}{\rho_{\text{H}^+ , \text{film}}} \tag{2.13}
\]

where \( \rho_{\text{H}^+ , \text{film}} \) is the resistivity of the ionomer in film form, which is equal to the values of \( \rho_{\text{mem}} \) shown in Figure 2.5 at the corresponding RH (at I/C ≥0.6/1 as was explained above) since the membrane and the ionomer are identical and have the same equivalent weight (EW). The thus obtained value of \( \tau(\varepsilon_i) \) vs. I/C-ratio is shown in Figure 2.9a. Within the experimental error in measuring both \( \rho_{\text{H}^+ , \text{cath}} \) and \( \rho_{\text{mem}} \), \( \tau(\varepsilon_i) \) is essentially one at the saturated RH conditions (i.e., 122% RH), analogous to what was observed by Boyer et al.
under saturated RH conditions. This suggests that the ionomer in the electrode forms a well-percolating proton conduction network and that the electrode proton resistivity can be estimated from Equation 2.11 by assuming $\tau(\varepsilon) \approx 1$. At lower RH values, $\tau(\varepsilon)$ remains near one for I/C-ratios $\geq 0.6/1$, but increases significantly at the lower I/C-ratios. Therefore, the proton conducting network formed at low ionomer volume fractions seems to be partially interrupted, and $\rho_{H^+,\text{cath}}$ has to be measured and cannot be simply estimated from Equation 2.11 using $\tau(\varepsilon) \approx 1$. The fact that the disruption of a percolating proton conduction network is a unique function of the ionomer volume fraction under the actual operating conditions can be illustrated more clearly by plotting $\tau(\varepsilon)$ versus the ionomer volume fraction at any given I/C-ratio and RH condition, shown in Figure 2.9b. This essentially implies that percolation of the ionomer network becomes imperfect as the effective film thickness of the ionomer on the catalyst (Pt and carbon) becomes too thin to maintain an uninterrupted network. The dependence of the ionomer volume fraction on RH is not commonly included in modeling estimates of proton conductivity, for example, in Ref. 18 or 30, but Figure 2.9 shows that this effect can have a significant impact on proton conductivity.
Figure 2.9: Tortuosity values obtained via Equation 2.10 versus (a) cathode I/C-ratio and versus (b) ionomer volume fraction at 35%, 50%, 75%, and 122% RH and 80°C in H₂/N₂. Data points represent independent measurement on different MEAs. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm² with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).
2.4.2 Electrode Proton Resistivity Validation – H$_2$/O$_2$ Measurements

The goal of this study is to predict MEA performance in H$_2$/O$_2$ under low-RH operating conditions using an electrochemical MEA/electrode model based on measured membrane and electrode proton resistivities. However, AC impedance spectra obtained in H$_2$/O$_2$ are complicated by the contributions from both the ORR charge transfer resistance and the variation of the electrode capacitance in the O$_2$-cathode potential region of ~0.6 to ~1V (see Figure 2.2). This makes it more difficult to properly quantify $R_{H^+,cath}$ from AC impedance measurements in H$_2$/O$_2$; therefore, we instead use the $R_{H^+,cath}$ vs. I/C-ratio and RH-level correlations obtained in H$_2$/N$_2$ shown in Figure 2.8. Considering that only 0.1A/cm$^2$ current density was applied and that the cell was operated at differential flow conditions, water production in the cathode will not significantly change the RH in the electrode and the membrane. Therefore, $\rho_{H^+,cath}$ and $HFR$ values measured in H$_2$/N$_2$ can be directly applied to model the H$_2$/O$_2$ data. If this assumption is valid, the cell voltages of cathodes with a wide range of I/C-ratios should yield the same value if corrected for $R_{DM/FF}$ and the proton conduction losses in membrane and electrodes, referred to as $E_{IR-free}$, even though the measured cell voltages, $E_{cell}$, vary significantly. The latter variation in $E_{cell}$ is shown in Figure 2.10, illustrating that cell voltages are nearly independent of I/C-ratio at high RH-levels, but significantly decrease with decreasing I/C-ratio at low-RH conditions, especially around and below the I/C ~0.6/1.
Figure 2.10: Dependence of cell voltage at 0.1 A/cm\(^2\) in H\(_2/O_2\) at 80°C on electrode’s I/C-ratio at 122%, 75%, 50% and 35% RH. Data points represent independent measurement on different MEAs. 50%Pt/V (Tanaka, Japan) at 0.4mg Pt/cm\(^2\) with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).

Previous work\(^{16}\) showed that the electrode performance at low RH can be described analytically under the assumption of negligible gas transport resistances, which is expected to be the case at low current densities using pure O\(_2\) or even with air operation if local relative humidities do not exceed 100%.\(^5\) Under these conditions, the cell voltage, \(E_{\text{cell}}\), is described by

\[
E_{\text{cell}} = E_{\text{rev}}(p_{\text{O}_2}, p_{\text{H}_2}, \text{RH}) - i \cdot HFR - \eta_{\text{HOR}} - \eta_{\text{ORR}} - i \cdot (R_{\text{eff}, \text{an}} + R_{\text{eff}, \text{cath}}) \tag{2.14}
\]
The reversible cell voltage, $E_{\text{rev}}$, is a function of temperature ($T$, in unit of K), partial pressure of H$_2$ ($p_{H_2}$, in unit of kPa), O$_2$ ($p_{O_2}$, in unit of kPa), and water vapor activity ($a_{H_2O}$) normalized to the corresponding reference O$_2$ and H$_2$ partial pressures ($p_{O_2}^*, p_{H_2}^*$) of 101.3 kPa, and a reference water vapor activity ($a_{H_2O}^* = 1$) corresponding to 100% RH (note that the water vapor activity is defined as the ratio of the actual water vapor pressure over the water vapor saturation pressure at the actual temperature). It can be calculated by the expression given in literature,$^{31}$ however adding the water vapor activity term which is required when considering low-RH conditions:

$$E^{\text{rev}}_{(p_{O_2}, p_{H_2}, \text{RH})} = 1.23 - 0.9 \times 10^{-3} (T - 298) + \frac{2.303 RT}{4F} \log \left( \frac{p_{H_2}}{p_{H_2}^*} \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^{a_{H_2O}} \right)$$

[2.15]

where $R$ is the universal gas constant (8.314 J·mol$^{-1}$·K$^{-1}$), $F$ is the Faraday constant (96485 C/mol), $a_{H_2O} / a_{H_2O}^* = 1$ for RH$\geq 100\%$, and $a_{H_2O} / a_{H_2O}^* \equiv RH$ (given as fraction rather than in %) at subsaturated condition.

In Equation 2.14 the $\eta_{\text{HOR}}$ is the overpotential for the HOR which is negligible for operation with pure H$_2$.\textsuperscript{8} Owing to the fast HOR kinetics, H$_2$ oxidation will occur very close to the anode/membrane interface, so that the effective resistance to proton conduction in the anode, $R^{\text{eff}}_{H^+, \text{an}}$, is only on the order of 15 mΩcm$^2$ even at 35% RH (see Ref. 5), translating into a negligible voltage loss of only about 1.5 mV at the 0.1 A/cm$^2$ in this study. These two terms will become significant only when operating at high current.
densities at very dry condition or at very low temperature.\textsuperscript{4, 5} \(\eta_{\text{ORR}}\) and \(R^{\text{eff}}_{H^{+},\text{cath}}\) are the overpotential for the ORR and the effective proton resistance in the cathode catalyst layer. The latter is defined as\textsuperscript{16}

\[
R^{\text{eff}}_{H^{+},\text{cath}} = \frac{R_{H^{+},\text{cath}}}{3 + \zeta}
\]  

[2.16]

where \(\zeta\) is a correction factor defined in Ref. 16, which can be calculated from the operating conditions and the electrode proton resistance. Omitting negligible terms and rearranging Equation 2.14 yields the true iR-free cell voltage, \(E_{iR-free}\)

\[
E_{iR-free} = E_{\text{cell}} + i \cdot HFR + i \cdot \left( \frac{R_{H^{+},\text{cath}}}{3 + \zeta} \right) = E^{\text{rev}}_{(P_{o_{2}}, P_{H_{2}}, \text{RH})} - \eta_{\text{ORR}}
\]  

[2.17]

The first two terms \(E_{\text{cell}} + i \cdot HFR\) in the middle of Equation 2.17 is commonly referred to as the ohmically corrected cell voltage, \(E_{\text{HFR-free}}\), determined via HFR measurements and represents the ohmic losses from proton conduction in the membrane, \(R_{\text{mem}}\), and from electronic contact resistances, \(R_{\text{DM/FF}}\). In the following, the associated voltage losses will be referred to as \(\Delta E_{\text{HFR}}\). On the other hand, the third term represents the current density dependent proton resistance (\(\zeta\) is a function of \(i\)), which leads to ohmic voltage losses in the electrode, referred to as \(\Delta E_{\text{electrode}}\). Figures 11a, b, c, and d show the measured cell voltages (diamonds), the HFR-corrected cell voltages, \(E_{\text{HFR-free}}\) (squares), and the fully ohmically corrected cell voltages, \(E_{iR-free}\) (triangles) versus cathode I/C-ratio at various RH conditions. Here, the difference between the measured cell voltage and \(E_{\text{HFR-free}}\) corresponds \(\Delta E_{\text{HFR}}\), while the difference between \(E_{\text{HFR-free}}\) and
$E_{IR-free}$ corresponds to $\Delta E_{electrode}$. The inset in each plot shows explicitly $\Delta E_{HFR}$ and $\Delta E_{electrode}$ at a given cathode I/C-ratio and RH. At 122%RH, the voltage loss caused by HFR ($\Delta E_{HFR}$) is dominant over ($\Delta E_{electrode}$) at all measured I/C-ratios. On the other hand, at all of the shown low-RH conditions, the performance loss due to $\Delta E_{electrode}$ exceeds that due to $\Delta E_{HFR}$ for I/C-ratios less than or equal to 0.6/1. Since the two terms of the right-hand-side of Equation 2.17 are independent of the electrode’s I/C-ratio, $E_{IR-free}$ is expected to be independent of the cathode I/C-ratio despite their strong effect on $E_{cell}$ (see Figure 2.10). Whether or not this is consistent with the experimental results is best illustrated by the data at 35% RH, where $E_{cell}$ dropped by ~200 mV at an I/C-ratio of 0.29/1 and by ~75 mV at an I/C-ratio of 0.39/1 in comparison to $E_{cell}$ at the highest I/C-ratio of 1.15/1 (see Figure 2.10). As seen in Figure 2.11d, the $E_{IR-free}$ voltage resulting from the resistance correction using $\Delta E_{electrode}$ and $\Delta E_{HFR}$, is indeed independent of the electrode’s I/C-ratio as expected except for the lowest value of 0.29/1, for which the largest cell voltage deviation of ~200 mV is reduced to <40 mV. This discrepancy at the lowest I/C-ratio is likely due to an inhomogeneous distribution of ionomer in the electrode, when the ionomer loading in the electrode approaches values where electrodes become structurally unstable due to the lack of ionomeric binder (note that the I/C-ratio of 0.29/1 was the lowest ratio at which structurally stable electrodes could be produced). Figure 2.12 is an overview of all the $E_{IR-free}$ data shown in Figure 2.11a-d. At all RH levels, the $E_{IR-free}$ voltage lies in a range of 888 ± 13 mV dictated by the two dashed lines at all I/C-ratios except the lowest one of 0.29/1 which has the largest scatter for the above mentioned reasons.
Figure 2.11: Dependence of (●) $E_{\text{cell}}$, (■) $E_{\text{HFR-free}}$, and (▲) $E_{\text{iR-free}}$ at 0.1 A/cm$^2$ in H$_2$/O$_2$ at 80°C on electrode’s I/C-ratio at (a) 122%RH, (b) 75%, (c) 50%, and (d) 35% RH. Data points represent independent measurement on different MEAs. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm$^2$ with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA). The inset in each plot shows $\Delta E_{\text{HFR}}$ (◊) and $\Delta E_{\text{electrode}}$ (Δ) at a given cathode I/C-ratio and RH.
Figure 2.12: An overview of the $E_{iR\text{-free}}$ values obtained vs. cathode I/C-ratio at various RH levels. Data points represent independent measurements on different MEAs. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm$^2$ with DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).

2.4.3 Effect of RH on $\eta_{\text{ORR}}$

While, as expected, the left-hand-side of Equation 2.17 was shown to be reasonably independent of the cathode I/C-ratio, the dependence of $\eta_{\text{ORR}}$ on RH on the right-hand-side of Equation 2.17 is less clear. Based on the literature, various dependencies of $\eta_{\text{ORR}}$ on RH were reported,\textsuperscript{32,33} but no rigorous account of the RH-induced proton conduction losses in the cathode had been made so far. In order to examine this aspect, we may rewrite Equation 2.17 as
\[
E_{\text{ir-free}} = E_{(P_{O_2}, P_{H_2}, RH)}^{\text{rev}} - \eta_{\text{ORR}(P_{O_2})}^{100\% RH} + \Delta \eta_{\text{ORR}(P_{H_2}, H^+)}^{x\% RH}
\]

where the \( \eta_{\text{ORR}(P_{O_2})}^{100\% RH} \) represents the ORR kinetics measured at 100% RH,\(^{10} \) while \( \Delta \eta_{\text{ORR}(P_{H_2}, H^+)}^{x\% RH} \) represents the changes in the ORR kinetics with RH from changes in water and proton activity. Due to the fact that the partial pressure of oxygen and hydrogen were kept constant for all experiments (see Experimental Section), the variation of \( E_{\text{ir-free}} \) comes from the well described RH-dependent variation of \( E_{(P_{O_2}, P_{H_2}, RH)}^{\text{rev}} \) (see Equation 2.15) and the unknown RH-dependence of the ORR kinetics, \( \Delta \eta_{\text{ORR}(P_{H_2}, H^+)}^{x\% RH} \). On the other hand, \( \eta_{\text{ORR}}^{100\% RH} \) remains constant, except for minor changes due to small variations from the nominal Pt loading of 0.4mgPt/cm\(^2\) (see Table 2.1). \( \eta_{\text{ORR}}^{100\% RH} \) at the current operating conditions can be calculated from Equation 2.19, which is obtained from Equations 3 and 4 in Ref. 10 at 80°C.

\[
\eta_{\text{ORR}}^{100\% RH} = \frac{2.303RT}{\alpha_c F} \log \left[ \frac{i + i_x}{10L_{Pt,cath} \cdot A_{Pt,el} \cdot i_{o,x}^* \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^\gamma} \right]
\]

where \( \alpha_c \) is the cathodic transfer coefficient with a determined value of, \( \alpha_c = 1 \),\(^{10} \) \( i_x \) is the H\(_2\) crossover current in unit of A/cm\(^2\), \( L_{Pt,cath} \) and \( A_{Pt,el} \) are the same as appeared in Equation 2.8, \( i_{o,x}^* \) (A/cm\(^2\)Pt) is the catalyst-specific exchange current density normalized to reference oxygen partial pressure (\( p_{O_2}^* \)) of 101.3 kPa at the reference temperature (\( T^* \)) of 80°C, and \( \gamma \) (0.54)\(^{10} \) is the kinetic reaction order with respect to oxygen partial.
pressure. Inserting Equations 2.15 and 2.19 into Equation 2.18, $E_{iR-free}$ can be expressed as

$$E_{iR-free} = 1.23 - 0.9 \times 10^{-3} (T - 298) + \frac{2.303RT}{4F} \log \left[ \frac{p_{H_2}}{p_{H_2}^*} \right]^2 \left( \frac{p_{O_2}}{p_{O_2}^*} \right) \left( \frac{a_{H_2O}}{a_{H_2O}^*} \right)^2$$

[2.20]

On the right-hand-side of Equation 2.20, the exchange current density under fully humidified conditions, $i_{o,s}^*$, and possible additional RH-induced overpotential losses, $\Delta \eta_{ORR(a_{H_2O},a_{H_2})}^{v_{RH}}$, are the only unknowns. By definition, the latter is zero under fully humidified conditions, in which case $i_{o,s}^*$ can be determined if all the ohmic losses can be quantified sufficiently accurately to obtain $E_{iR-free}$ (left-hand-side of Equation 2.20) from the measured cell voltages. $E_{iR-free}$ values at oversaturated conditions for the entire range of I/C-ratios have already been shown in Figure 2.12, allowing for a precise quantification of $i_{o,s}^*$ via Equation 2.20 (note that $\Delta \eta_{ORR(a_{H_2O},a_{H_2})}^{v_{RH}}$ is zero in this case).

The thus obtained exchange current densities, $i_{o,s}^*$, are listed in Table 2.1, together with the determined specific activities, $i_s^{(0.9V)}$ (A/cm²Pt), and mass activities, $i_m^{(0.9V)}$ (A/mgPt), at 0.9 V (at the reference reactant partial pressures of 101.3 kPaabs and the reference temperature of 80°C). The average values of these kinetic parameters measured on our 50% Pt/Vulcan catalyst and its average in-situ surface area, $A_{Pt,el}$ (m²/gPt), are shown in
Table 2.2 (second column) and are compared to published data on a 47%wt. Pt/Vulcan catalyst (see third column in Table 2.2), showing excellent agreement. On the other hand, slightly higher ORR activity is reported for a 47%wt. Pt/C catalyst (see fourth column in Table 2.2), which is likely due to higher Pt dispersions of this catalyst.

Table 2.2: Average values of catalyst surface area, $A_{Pl,el}$, and ORR kinetic parameters ($i_s^{0.9V}$, $i_m^{0.9V}$, and $i_{o,s}$) for the MEAs shown in Table 2.1 and comparison to literature values. All kinetic parameters at 0.9 V are normalized to reference conditions of $T^*=80$°C, $\geq 100\%$ RH, and $p_{H_2}^* = p_{O_2}^* = 101.3$ kPaabs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>50% Pt/Vu (TKK, this work)</th>
<th>47% Pt/Vu (JM)$^8$</th>
<th>47% Pt/C (TKK)$^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{Pl,el}$ [m$^2$/gPt]</td>
<td>46±3</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>$i_s^{0.9V}$ [A/cm$^2$ Pt]</td>
<td>1.5 ± 0.2 ×10$^{-4}$</td>
<td>1.4×10$^{-4}$</td>
<td>1.8×10$^{-4}$</td>
</tr>
<tr>
<td>$i_m^{0.9V}$ [A/mgPt]</td>
<td>0.07 ± 0.01</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>$i_{o,s}$ [A/cm$^2$ Pt]</td>
<td>1.5 ± 0.2 ×10$^{-8}$</td>
<td>1.4×10$^{-8}$</td>
<td>1.7×10$^{-8}$</td>
</tr>
</tbody>
</table>

Using the above determined exchange current density, Equation 2.20 now allows the calculation of the iR-free voltages (right-hand-side of Equation 2.20) in the case where $\Delta \eta_{ORR(s_H + a_H)}^{v%H}$ is arbitrarily assumed to be zero at any of the measured RH level. These calculated $E_{iR-free}$ values with assumed RH-independent ORR kinetics (i.e., $\Delta \eta_{ORR(s_H + a_H)}^{v%H} = 0$) are shown in Figure 2.13 (diamonds) together with the experimentally determined $E_{iR-free}$ values (open squares) which were taken from Figure 2.12. Each data point in Figure 2.13 represents the average value of 12 MEAs with I/C-ratios ranging from 0.39/1 to 1.15/1, and the error bars indicate the standard deviation of these 12 independent measurements (note that the error bars for the calculated values (diamonds) results from the small variation of Pt-loading for the 12 MEAs (see Table 2.1)). To avoid
introducing unexpected errors, the electrodes at I/C of 0.29/1 were not included in Figure 2.13 because they are at the threshold of being able to make good electrodes as stated earlier which caused too much scatter in cell performance at subsaturated conditions as shown in Figure 2.12.

![Figure 2.13: Comparison of $E_{iR\text{-free}}$ values](image)

**Figure 2.13:** Comparison of $E_{iR\text{-free}}$ values calculated from Equation 2.20 assuming $\Delta \eta_{\text{orr, H}_2O}$ = 0 (diamonds) and experimentally determined $E_{iR\text{-free}}$ values (open squares) vs. RH (note that data points at 122% RH were placed at 100% RH, since thermodynamically values above 100% RH are equivalent to 100% RH). Each data point represents the average value of 12 samples with the I/C-ratio ranging from 0.39/1 to 1.15/1. 50%Pt/V (Tanaka, Japan) at 0.4mgPt/cm$^2$ with DE2021$^\text{®}$ ionomer (DuPont, USA), NRE211$^\text{®}$ membrane (DuPont, USA). Error bars represent one standard deviation.

Obviously, the experimentally obtained resistance-corrected voltages, $E_{iR\text{-free}}$, are independent of RH at subsaturated condition, but a ~9 mV higher $E_{iR\text{-free}}$ value is obtained at fully humidified conditions. The reason for this difference is not clear, however it
should be noted that this difference is rather small. On the other hand, the calculated $E_{iR-free}$ using Equation 2.20 and assuming $\Delta \eta_{ORR(a_{H_2O}, a_{H^+})}^{x\%RH} = 0$ increases continuously with decreasing RH, indicating that $\Delta \eta_{ORR(a_{H_2O}, a_{H^+})}^{x\%RH}$ indeed increases with decreasing RH or, in other words, that lowering the RH slightly reduces the ORR kinetics. This is shown more clearly in Figure 2.14, plotting the voltage difference between the two lines in Figure 2.13 vs. RH, which corresponds to $\Delta \eta_{ORR(a_{H_2O}, a_{H^+})}^{x\%RH}$ vs. RH, whereby the error bars represent the root mean squared standard deviations of the theoretical (i.e., $\Delta \eta_{ORR(a_{H_2O}, a_{H^+})}^{x\%RH} = 0$) and experimental $E_{iR-free}$ values in Figure 2.13.

![Graph showing RH-induced kinetic ORR overpotential losses vs. RH.](image)

**Figure 2.14**: RH-induced kinetic ORR overpotential losses, $\Delta \eta_{ORR(a_{H_2O}, a_{H^+})}^{x\%RH}$, vs. RH. Each data point is the averaged difference between the calculated $E_{iR-free}$ values (assuming $\Delta \eta_{ORR(a_{H_2O}, a_{H^+})}^{x\%RH} = 0$, see Equation 2.18) and the measured $E_{iR-free}$ values of 12 MEAs with I/C-ratios ranging from 0.39/1 to 1.15/1. The error bar represents the root mean squared standard deviation of the voltage difference between the two lines shown in Figure 2.13.
There’s an obvious trend that the determined \( \Delta \eta^{\% RH}_{\text{ORR}(a_{H_2O},a_{H^+})} \) values become more negative with decreasing RH, ranging from 0 to -25mV. This voltage range between 35% RH and fully humidified conditions is consistent with results reported by Neyerlin et al.,\(^\text{32}\) even though their variation of \( \Delta \eta^{\% RH}_{\text{ORR}(a_{H_2O},a_{H^+})} \) with RH is slightly different. Nevertheless, at any given RH-level, the difference there is only ca. ~10mV discrepancy which is small and is probably due to the fact that in their work the proton resistance was predicted from a model assuming a tortuosity of one, which may have led to some small errors despite their use of very thin and conductive electrodes. On the other hand, much larger effects of RH on ORR kinetics in PEMFCs were reported by Xu et al.,\(^\text{33}\) with a value of \( \Delta \eta^{\% RH}_{\text{ORR}(a_{H_2O},a_{H^+})} \sim 100 \) mV at 0.1A/cm\(^2\) and 35%RH at 120°C, significantly larger than the value of ca. -25 mV in Figure 2.14. Considering the large ohmic losses in the cathode, \( \Delta E_{\text{electrode}} \), at low RH (see insets in Figure 2.11), it is likely that this much larger \( \Delta \eta^{\% RH}_{\text{ORR}(a_{H_2O},a_{H^+})} \) value in their work is due to not considering this term when extracting ORR kinetic parameters. This is confirmed by their later report\(^\text{34}\) showing that when the loss from electrode proton conduction was considered, the effect of RH on the ORR kinetics is reduced to around -50mV instead of -100mV at 35%RH and 120°C as reported in their previous work.\(^\text{33}\) Essentially zero \( \Delta \eta^{\% RH}_{\text{ORR}(a_{H_2O},a_{H^+})} \) was obtained by Murthi et al.\(^\text{35}\) in a model study using at Pt/C thin-film rotating disk electrode measurement in 1 molar (\( \lambda \sim 50 \)) and 6 molar (\( \lambda \sim 4 \)) triflic acid, where no difference in catalyst activity was observed. In summary, the RH-induced ORR kinetic losses are indeed very small, only ca. -25mV at 35%RH in our study, while the losses from electrode proton conduction could reach ~200mV at the same conditions for an electrode at I/C-ratio of 0.29/1. In
order to obtain the RH-induced ORR kinetic losses, all of the ohmic resistance losses in
the electrode have to be considered accurately, i.e., when considering $E_{iR-free}$ rather than
$E_{HFR-free}$.

2.5 SUMMARY

An AC impedance method was developed to quantify the through-plane RH-dependent membrane resistance and the cathode proton resistance in a H$_2$/N$_2$ cell with the assumption that the proton resistance and the pseudo-capacitance are distributed uniformly throughout the electrode. The measured resistance data can be applied to rather accurately predict the performance of a H$_2$/O$_2$ cell, provided that local RH-values in the membrane and the electrode are known, which a the case for low current densities, where RH-gradients between the flow-field channels and the electrode/membrane are negligible. Properly accounting for ohmic losses in the cathode, it was found that the RH-induced effect on the ORR kinetics is rather small, corresponding to kinetic voltage losses of less than 25 mV at 35% RH.

It is found that the electrode tortuosity is a strong function of electrode I/C-ratio when its value is below 0.6/1; hence, for advanced MEA performance models, the electrode proton resistivity vs. RH represents an intrinsic electrode property and must be determined via, for example, the AC impedance method proposed in this study. For the model electrodes used in this study, there is a threshold for proton conduction in the electrode at an ionomer volume fraction of ~13% in the electrode at all RH levels. Above this threshold, the ionomer-network in the electrode is characterized by a tortuosity of ~1 within a wide range of RH. On the other hand, below this threshold, the tortuosity is a
strong function of ionomer volume fraction. This implies that high electrode I/C-ratios (I/C-ratio≥0.6/1) are necessary for cells operating at low-RH conditions to avoid significant voltage losses from high electrode proton resistances.

Although under fully humidified conditions the $E_{iR\text{-free}}$ voltages are ~9mV higher than those at subsaturated conditions, the difference is rather small. Therefore, it is reasonable to conclude that the $E_{iR\text{-free}}$ voltages are essentially independent of cathode I/C-ratio and RH. This strongly suggests that the measured membrane and electrode proton resistivities indeed represent intrinsic membrane and electrode properties, respectively. Clearly, the cathode proton resistivities extracted from the AC impedance spectra are critical electrode properties which are required for voltage loss quantification and cell performance predictions.

**SYMBOLS**

- $A$: MEA active area, cm$^2$
- $A_{Pt,el}$: in situ specific Pt surface area in the electrode of an MEA, m$^2$Pt/gPt
- $a_H^+$: proton activity
- $a_{H_2O}$: water activity
- $a_{H_2O}^*$: reference water activity, assigned an arbitrary value of 1 at RH≥100%
- $C_{cath}$: cathode capacitance, F/cm$^2_{MEA}$
- $C_i$: capacitance of an infinitesimal electrode slice, F/cm$^2_{MEA}$
- $C_{specific}$: Pt-specific capacitance, mF/cm$^2_{Pt}$
- $d_{I, dry}$: density of dry ionomer, g/cm$^3$
- $d_{mem, dry}$: density of dry membrane, g/cm$^3$
- $d_w$: density of water, g/cm$^3$
\[ \Delta E_{\text{electrode}} \] ohmic voltage loss in electrode, V

\[ \Delta E_{\text{HFR}} \] ohmic voltage loss from high frequency resistance, V

\[ E_{\text{HFR-free}} \] observed cell voltage corrected by high frequency resistance, V

\[ E_{\text{iR-free}} \] iR-free cell voltage, observed cell voltage plus corrections from proton resistance in the cathode and high frequency resistance, V

\[ E_{\text{rev}}^{(\text{P}_{\text{O}_2}, \text{P}_{\text{H}_2}, \text{RH})} \] reversible cell potential (function of T, \( \text{P}_{\text{H}_2} \), \( \text{P}_{\text{O}_2} \), RH), V

\[ f \] frequency, Hz

\[ f_t \] factor for electrode thickness calculation, 28\pm2\mu m/(mgC/cm^2)

\[ F \] Faraday constant, A-s/equiv

\[ i \] current density, A/cm^2

\[ i_{m}^{*(0.9V)} \] mass-specific current density measured at a constant iR-free cell voltage of 0.9V as a function of temperature and oxygen and hydrogen partial pressure, A/mgPt

\[ i_{o,s}^{*} \] exchange current density referenced to 80°C and 101.3 kPa of oxygen partial pressure, based on Pt surface area, A/cm^2_{Pt}

\[ i_{s}^{*(0.9V)} \] specific current density measured at a constant iR-free cell voltage of 0.9V as a function of temperature and oxygen and hydrogen partial pressure, A/mgPt

\[ i_{x} \] current density associated with H2 crossover (crossing through the membrane), A/cm^2

\[ L_{\text{Pt,cath}} \] cathode Pt loading of the MEA, mgPt/cm^2

\[ m_{C} \] carbon loading in the electrode, mgC/cm^2

\[ m_{I} \] ionomer loading in the electrode, g

\[ M_{w} \] water molecular weight, 18g/mol

\[ \text{P}_{\text{H}_2} \] H2 partial pressure, kPa

\[ \text{P}_{\text{H}_2}^{*} \] reference H2 partial pressure, 101.3 kPa

\[ \text{P}_{\text{O}_2} \] O2 partial pressure, kPa

\[ \text{P}_{\text{O}_2}^{*} \] reference O2 partial pressure, 101.3 kPa

\[ R \] universal gas constant, J-mol^{-1}.K^{-1}

\[ R_{\text{ct,l}} \] charge-transfer resistance of the electrochemical reactions in the electrode, \( \Omega \cdot \text{cm}^2 \)
\( R_{DM/FF} \) compression-dependent contact resistance between the flow field and diffusion media, \( \Omega \cdot \text{cm}^2 \)

\( R_{\text{electronic}} \) electronic resistance of the cell, \( \Omega \cdot \text{cm}^2 \)

\( R_{H^+, \text{cath}} \) proton resistance in the cathode, \( \Omega \cdot \text{cm}^2 \)

\( R_{H^+, \text{cath}, i} \) incremental proton resistance in the cathode, \( \Omega \cdot \text{cm}^2 \)

\( R_{H^+, \text{cath}}^{\text{eff}} \) effective proton resistance in the cathode, \( \Omega \cdot \text{cm}^2 \)

\( R_{\text{mem}} \) membrane resistance, \( \Omega \cdot \text{cm}^2 \)

\( T \) temperature, K or °C

\( t_{\text{cath}} \) thickness of cathode catalyst layer, cm

\( t_{\text{mem}} \) thickness of membrane as a function of temperature and RH, cm

\( \Delta t_{\text{mem}} \) change of membrane thickness as a function of temperature and RH, cm

\( V_{\text{cath}} \) volume of cathode catalyst layer, cm³

\( V_I \) volume of ionomer as a function of RH, cm³

\( V_{\text{mem}} \) volume of membrane as a function of temperature and RH, cm³

\( \Delta V_{\text{mem}} \) change of membrane volume as a function of temperature and RH, cm³

Greek

\( \alpha_c \) cathode transfer coefficient

\( \epsilon_i \) ionomer volume fraction in cathode

\( \gamma \) ORR order with respect to \( \text{O}_2 \) partial pressure at constant overpotential

\( \eta_{\text{HOR}} \) overpotential of the HOR, V

\( \eta_{\text{ORR}} \) overpotential of the ORR, V

\( \eta_{\text{ORR}}^{100\% \text{RH}} \) overpotential of the ORR at 100%RH, V

\( \Delta \eta_{\text{ORR}(\text{at}100\% \text{RH})}^{x\% \text{RH}} \) change in overpotential of the ORR at x%RH with respect to water and proton activities, referenced to water and proton activities at 100%RH, V

\( \lambda \) number of water molecules per proton as a function of RH

\( \kappa_{(T, RH)} \) proton conductivity in the cathode (function of T, RH), S/cm

\( \rho_{H^+, \text{cath}} \) proton resistivity in the cathode, \( \Omega \cdot \text{cm} \)
$\rho_{mem}$ membrane proton resistivity, $\Omega \cdot \text{cm}$

$\tau_{i}$ tortuosity of ionomer (proton conduction) in the catalyst layer (function of ionomer volume fraction)

$\zeta$ correction factor for reduced cathode proton transport length to membrane

**REFERENCES**


Chapter 3

Proton Conduction in PEM Fuel Cell Cathodes: Effects of Electrode Thickness and Ionomer Equivalent Weight

3.1 INTRODUCTION

The proton resistivity within a H₂/O₂ proton exchange membrane (PEM) fuel cell electrode, $\rho_{H^+,\text{electrode}}$, is an important design parameter for membrane electrode assembly (MEA), as it controls catalyst utilization, particularly under low relative humidity (RH) conditions.¹ When using pure H₂ (not reformate), the extent of catalyst utilization is not very critical for the H₂ oxidation reaction (HOR) in anode due to its fast kinetics,² however, it is highly critical for the cathode O₂ reduction reaction (ORR) with its 7 order of magnitude slower kinetics.³ The resistivity to proton conduction in the cathode, $\rho_{H^+,\text{cath}}$, is generally an MEA performance controlling factor, while the influence of $\rho_{H^+,\text{an}}$ is usually negligible except drawing large current densities at very low RH and at low temperature during freeze startup.⁴,⁵ Therefore, in the present work, we have focused on evaluating the proton resistivity of various PEM cathodes; nevertheless, the methodology and the resulting proton resistivity relationships are valid whether an electrode is used as the cathode or as the anode.

In Chapter 2, the cathode proton resistivity was shown to depend on the electrode’s ionomer to carbon weight ratio (I/C-ratio) as well as on the relative humidity.⁶,⁷ Furthermore, it was shown that the measured $\rho_{H^+,\text{cath}}$ could be used to predict MEA
performance over a wide range of I/C-ratios and RH, which led to the conclusion that
$\rho_{H^+,\text{cath}}$ is indeed an intrinsic electrode property. This implies that for uniform electrodes
(the ionomer covers the catalyst throughout the electrode), $\rho_{H^+,\text{cath}}$ should be independent
of electrode thickness and Pt weight percentage on the carbon support, as long as the
same electrode components (ionomer and carbon-support type) and I/C-ratio are used.
The current study further verifies that the experimental method for measuring the
electrode proton resistance and its use for predicting electrode performance\textsuperscript{6,7} can be used
for a wide range of electrode types and electrode thicknesses. Since the equivalent weight
(EW, in unit of g\textsubscript{polymer}/mol\textsubscript{SO\textsubscript{3}H}) or the ion exchange capacity (IEC, in unit of meq/g) of
the ionomer affects its proton conductivity,\textsuperscript{8-13} using ionomers with different EW (or
IEC) and measuring their corresponding electrode’s proton resistance can give us a better
understanding of the impact of the ionomer bulk proton resistivity on the electrode proton
resistivity. The method to determine EW and IEC is described in Ref. 14. In this work,
EW is used to represent the ionomer’s proton conduction capacity, as the inverse of the
EW multiplied by 1000 is equivalent to IEC.

While previous electrodes were made with 1050 EW ionomer,\textsuperscript{6,7} the present work
employs electrodes made with an ionomer of lower EW at 850. Lower electrode proton
resistivities are expected for electrodes made with low EW ionomers at the same I/C, and
better cell performance should be obtained as shown in some publications under low RH
condition,\textsuperscript{15-17} where large proton resistances can strongly reduce MEA performance. In
the present work, the electrode proton resistivity is measured with AC impedance spectra
and its impact on fuel cell performance is further investigated.
3.2 EXPERIMENTAL

Membrane Electrode Assemblies (MEAs)

MEAs with 50 cm$^2$ active area were fabricated with DuPont DE2021® 1050 equivalent weight (EW) ionomer by hot pressing electrode decals onto 25 µm thick Nafion-211® membranes (DuPont, USA, 1050EW). The anode Pt loading was kept at about 0.4 mg$_{Pt}$/cm$^2$. All anodes had an I/C-ratio of ~0.9/1. The cathodes were fabricated using either a ~50%wt. or 20%wt. Pt/Vulcan catalyst (Tanaka, Japan). The cathode inks were prepared using isopropanol (IPA)/H$_2$O (3/1 weight ratio) solvent with 6 wt% carbon content. The Pt loading in cathodes was varied from 0.05 to 0.4 mg$_{Pt}$/cm$^2$ at various I/C-ratios. In order to study the ionomer EW impact on the electrode proton resistivity, the DuPont DE2029® 850 EW ionomer was used to fabricate a comparison series of electrodes with ~50%wt. Pt/Vulcan catalyst.

Scanning Electron Microscopy (SEM)

A Carl Zeiss SMT - An Ultra 55 field emission (FE)-SEM was used to observe the electrode and recast membrane thickness. The SEM samples were cut randomly from the MEAs and prepared by freeze fracture at liquid N$_2$ temperature to get clean cross sectional surfaces. The SEM images were taken using an accelerating voltage of 2.0 kV and an in-lens secondary electron imaging mode.

Titration

The exact ionomer EWs were determined by a titration procedure described as the following. 0.2-0.4g 20%wt. ionomer solution (DuPont, USA) is added in a titration cup
and about 40mL 0.1N NaCl solution is added later. The titration is performed with a Mettler Toledo DL12 titrator with standard 0.01N NaOH solution and Phenol Red as the pH indicator. The densities of the dry membranes recast from the ionomer solution were determined based on the titration results by subtracting the weight of the absorbed water.

**Conductivity of Recast Membranes**

The membranes used for determining the ionomer bulk conductivity were prepared by casting the corresponding as-received ionomer solution on a glass plate at room temperature and dried overnight. All of the cast membranes were then annealed at 130°C for 4 hrs before assembling with electrodes. Both membranes had a thickness of ~20 μm at room temperature and ambient environment, and they were incorporated into MEAs for membrane conductivity characterization using AC impedance. It should be noted that when the membrane resistivity is applied, the increase of membrane thickness due to water uptake and swelling is considered (assuming swelling only in thickness direction due to x/y constraint\(^{18, 19}\)). The anodes were the same for \(\rho_{H^+,\text{cath}}\) measurements, and the cathodes were fabricated using ~50%wt. Pt/V and DE2021® 1050EW ionomer with an I/C of 0.8/1 at ~0.4 mgPt/cm² Pt loading.

**AC impedance and Cell Performance**

AC impedance spectra and cell performance were acquired with a Zahner iM6e (Zahner Inc. Germany). In H\(_2\)/N\(_2\) experiments, the cell was potentiostated at +0.2 V, with a peak-to-peak perturbation of 2 mV at frequencies ranging from 0.5 to 20,000 Hz. Five spectra were collected at each condition to verify reproducibility. Each electrode’s cell performance in H\(_2\)/O\(_2\) was conducted at 0.1 A/cm\(^2\) and the voltage data points are
averaged values over 25min time span subsequent to precondition for 15 min at 0.1A/cm². All experiments were conducted at 80°C with four different inlet/outlet RH-values under differential flow conditions (i.e., negligible RH gradients). H₂ and O₂ partial pressures at each RH-level were maintained at 253 kPa(abs) (at the cell outlet) by varying the total cell pressure: 300 kPa(abs) at 122%RH, 287 kPa(abs) at 75% RH, 276 kPa(abs) at 50% RH, and 269 kPa(abs) at 35% RH. H₂ flow rates were held constant at 2100 sccm (standard cubic centimeter per minute), while O₂ and N₂ flow rates were held constant at 1750 sccm.

3.3 RESULTS AND DISCUSSION

3.3.1 Proton Resistivity: Independent of Electrode Thickness and Pt-loading

Electrode proton resistance was measured by AC impedance technique and analyzed by fitting high frequency resistance (HFR, Ω·cm²), electrode proton resistance (RH⁺,cath, Ω·cm²) and cathode capacitance (Ccath, F/cm²) to a transmission-line model.⁷ A sample impedance spectrum is shown in Figure 3.1, which includes the experimentally determined AC-impedance and a model fit to the data.
Figure 3.1: Comparison of data obtained in H$_2$/N$_2$ at 0.2 V (75%RH, 80°C) with the transmission-line model. Cathode I/C-ratio=0.39/1, Pt-loading= 0.4mg/cm$^2$ with 50%Pt/V (Tanaka, Japan) and DE2021® ionomer (DuPont, USA), NRE211® membrane (DuPont, USA).

As seen in Figure 3.1, the HFR can be read from the real axis intercept with the impedance by extrapolating the high frequency end to the real axis. There is a 45° segment in the spectrum, which will provide the information to obtain a ratio of electrode proton resistance over its capacitance. The ratio can be expressed by

$$\frac{R_{H^+\text{cath}}}{C_{\text{cath}}} = \left[Im(Z)\right]^2 \cdot 4 \cdot \pi \cdot f \equiv \left[Re(Z)\right] - HFR \cdot 4 \cdot \pi \cdot f$$  \[3.1\]
where $Im(Z)$ is the imaginary part of the impedance ($\Omega\cdot\text{cm}^2$), $f$ is the corresponding frequency (Hz) and $Re(Z)$ is the real part of the impedance ($\Omega\cdot\text{cm}^2$). Therefore, this ratio is only determined by the impedance response of the specific electrode with certain composition at certain operating conditions. $C_{\text{cath}}$ can be obtained by:

$$C_{\text{cath}} = \lim_{f \to 0} \left[ \frac{-1}{2 \cdot \pi \cdot f \cdot Im(Z)} \right]$$

[3.2]

Once $C_{\text{cath}}$ is available, $R_{H^+,\text{cath}}$ is readily determined by Equation 3.1. All the obtained impedance spectra in this section and the next section are analyzed by the above described method (see details in Ref. 6,7).

In the previous work, $R_{H^+,\text{cath}}$ of uniform electrodes with the same nominal thickness ($\sim12$ $\mu$m) at various I/C-ratios was evaluated at various RHs. It was concluded that $\rho_{H^+,\text{cath}}$ at any given RH is an I/C-ratio dependent electrode property, implying that it should only depend on electrode composition and that it should be independent of electrode thickness and Pt-loading. Quite clearly, using the same catalyst, the electrode thickness is proportional to the Pt-loading per unit projected area, and electrodes fabricated with $\sim50\%$wt. Pt/Vulcan catalyst at nominal loadings of 0.1, 0.2, and 0.4 mg-Pt/cm$^2$ have a thickness of 3, 6, and 12 $\mu$m, respectively. Fundamentally, it was shown that the electrode thickness for catalysts based on Vulcan or Kejten black supports and for I/C-ratios of $<3/1$ only depends on the carbon loading of the electrode, so that the cathode thickness, $t_{\text{cath}}$, can be calculated from the carbon loading multiplied by 28 $\mu$m/(mgC/cm$^2$ electrode), consistent with the thicknesses shown in Ref. 20. Therefore, electrodes fabricated with 20%wt. Pt/Vulcan catalyst at nominal loadings of 0.05, 0.1,
and 0.2 mg-Pt/cm$^2$, resulted in electrode thicknesses of 6, 12, and 24 μm, respectively. To further confirm the correlation between electrode thickness and carbon loading, randomly selected samples were cross sectioned and checked under FE-SEM for the actual electrode thickness. Figures 3.2 a-c shows the SEM images for various cathode thicknesses (dictated by the dashed white lines in each of the images) by varying the Pt-loading per area of MEA and Pt-loading on carbon support (~50% or 20%w.t.) at I/C of 0.6. Table 3.1 lists the details of each sample including the Pt-loading, measured cathode thickness and the calculated correlation factor ($f_t$) based on the measured $t_{cath}$ and cathode carbon-loading. Column 7 showed that $f_t$ varies from 27 to 31, which matches quite well with the reported value of 28±2μm/(mgC/cm$^2$ electrode).$^4$
Figure 3.2: SEM images of electrodes (I/C=0.6) with various thicknesses by varying Pt loading, Pt weight percentage on carbon support. Measured cathode thickness of samples are (a): 4.1µm, (b): 14.2µm and (c): 11.3µm. Cathodes of samples A and B are made with ~50%w.t. Pt/V, and the Pt-loadings are 0.120 mg/cm² and 0.443 mg Pt/cm², respectively. Cathode of sample C is made with ~20%w.t. Pt/V and Pt-loading of 0.089 mg Pt/cm². SEM images were taken under in-lens secondary electron under 2.0kV energy mode.

Table 3.1: Cathode properties of sample MEAs (Figures 3.2 a-c) showing the measured electrode thickness and the obtained correlation factor $f_t$ between electrode carbon loading and $t_{cath}$. All MEAs use 1050EW (DE2021) ionomer, and Pt/Vulcan catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt loading [mgPt/cm²]</th>
<th>%wt. Pt on carbon</th>
<th>C loading [mgC/cm²]</th>
<th>Measured $t_{cath}$ [µm]</th>
<th>Calculated $f_t$ [µm/(mgC/cm²)]</th>
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<td>0.141</td>
<td>4.1</td>
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<tr>
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<tr>
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<td>19.7</td>
<td>0.363</td>
<td>11.3</td>
<td>31</td>
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</table>
Though the actual electrode thickness can be determined by SEM, in all cases, the electrode thickness values used in the following proton resistivity calculations are estimated based on the above correlation between electrode carbon loading and thickness.

Table 3.2 summarizes the cathode properties of the MEAs used in this study, including Pt loading, I/C-ratio, and electrode thickness.

<table>
<thead>
<tr>
<th>I/C-ratio</th>
<th>Pt loading [mgPt/cm²]</th>
<th>% wt. Pt on carbon</th>
<th>C loading [mgC/cm²]</th>
<th>t_cath [μm]</th>
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<tr>
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Table 3.2: Cathode Pt-loading, Pt %w.t. on carbon, carbon loading and calculated t_cath for MEAs appeared in Figure 3.3a-3.3b. All MEAs use 1050EW (DE2021) ionomer, and Pt/Vulcan catalyst.
Electrodes with two I/C-ratios, 0.6 and 0.8, prepared with either 50%wt Pt/C and 20%wt Pt/C catalyst were studied in this work. Figures 3.3a and 3.3b show $\rho_{H^+,cath}$ of cathodes with I/C-ratio at 0.6 and 0.8 at 122%, 75%, 50%, and 35%RH respectively. For electrodes with I/C-ratio at 0.6, the electrode thickness varies from 5 $\mu$m to 17 $\mu$m, and for I/C=0.8 electrodes, the electrode thickness changes from 2.5 $\mu$m to 18 $\mu$m. As shown in the plots, $\rho_{H^+,cath}$ is indeed an intrinsic electrode property independent of electrode thickness and Pt-loading at both I/C-ratios. In Figure 3.3b, some points at 75%RH and 122%RH are not available at $t_{cath}=2.5\mu$m because the resistances at those conditions are too small to be accurately determined. The thickest electrodes studied in this work are at about 18 $\mu$m prepared with 20wt% Pt/C. Though the $\rho_{H^+,cath}$ values extracted from impedance spectra for the thickest electrodes are a little bit higher than the thinner ones, especially at 35%RH conditions, the difference is <20% for electrodes at I/C-ratio of 0.6 and <14% for electrodes at I/C-ratio of 0.8 from the corresponding average $\rho_{H^+,cath}$ value lines in the plots. Therefore, the measurement of the proton resistance is still feasible and reasonably accurate within the error of the electrode thickness and the impedance measurement.
Figure 3.3: Electrode proton resistivity dependence on the electrode thickness and Pt-loading in H₂/N₂ at 80°C, 122%, 75%, 50%, and 35% RH. Each point represents one individual MEA. Plot (a): I/C-ratio=0.6 and plot (b): I/C-ratio=0.8. Dashed lines represent the average electrode proton resistivity at each condition.
3.3.2 Dependence of $\rho_{H^+,\text{cath}}$ on Ionomer Equivalent Weight (EW)

Two series of electrodes with different EW ionomers were fabricated to study the ionomer EW effect on electrode proton resistivity. Using the titration procedure described in experimental section, the true EWs were determined as 893 for ionomer DE2029® (850 from manufacturer) and 1042 for ionomer DE2021® (1050 from manufacturer). The following data analysis will be based on the actual ionomer EW even though the old names are used. Figure 3.4 shows the $\rho_{H^+,\text{cath}}$ of electrodes with 1050 EW ionomer or 850 EW ionomer. The data for the 1050 EW ionomer electrodes are the same as those previously reported,⁶,⁷ and the electrodes components are given in Table 1 in Ref. 7 or Table 2.1 in Chapter 2. The cathode components for the electrodes with 850EW ionomer are listed in Table 3.3. The electrodes made with lower EW ionomer, at the same I/C-ratio, are expected to have lower resistivity under all RH levels. Lower $\rho_{H^+,\text{cath}}$ values are indeed obtained for the low EW ionomer electrodes, although the difference in $\rho_{H^+,\text{cath}}$ between these electrodes with different EW disappears at I/C>0.8. Using SEM we examined the electrode thicknesses to verify the thickness used to calculate $\rho_{H^+,\text{cath}}$. Figures 3.5a and 3.5b show the thickness of cathodes with 850EW and 1050EW ionomers at I/C-ratio of 1, respectively. The carbon loading of a sample 850EW cathode shown in Figure 3.5a is 0.487mg/cm², and using $f_t=28\mu$m/(mgC/cm²) the calculated thickness of 13.6µm is consistent with the thickness of 13.4µm obtained by SEM; similarly, the carbon loading of a sample 1050EW cathode shown in Figure 3.5b is 0.452 mg/cm², and the calculated thickness of 12.7µm agrees well with the SEM measured thickness of 12.4µm. This confirms that the correlation between electrode carbon loading
and thickness, namely $f_t = 28 \mu m/(mg_c/cm^2)$, still holds for the 850EW ionomer electrodes, as one might expect. Therefore, the anomaly observed at high I/C value in Figure 3.4 is not a measurement or calculation artifact.

**Figure 3.4**: Dependence of the electrode proton resistivity on the cathode ionomer EW at 122%, 75%, 50%, and 35%RH in H$_2$/N$_2$ at 80°C. Dashed lines indicated the resistivity obtained for 850 EW electrodes while solid lines represent the resistivity obtained for 1050 EW electrodes. Data points represent independent measurements on different MEAs.
Table 3.3: Cathode Pt loading, carbon-loading and calculated $t_{\text{cath}}$ for MEAs (with 850EW ionomer and 46% Pt/C) appeared in Figure 3.4. The information for MEAs with 1050EW ionomer is given in Ref. 7 (see details in Table 1) or Table 2.1 in Chapter 2.

<table>
<thead>
<tr>
<th>I/C-ratio</th>
<th>Pt loading [mg Pt/cm$^2$]</th>
<th>C loading [mg C/cm$^2$]</th>
<th>$t_{\text{cath}}$ [μm]</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td></td>
<td>0.331</td>
<td>0.415</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Figure 3.5: SEM images of cathodes with ~50%w.t. Pt/V catalyst and (a): 850EW and (b): 1050EW ionomers. Measured cathode thicknesses are (a): 13.4μm and (b): 12.4μm. SEM images were taken under in-lens secondary electron under 2.0kV energy mode.
It needs to be noted that ionomers with different EW result in different sulfonic acid group concentrations per unit volume of electrode at the same I/C. This can be quantified by a new term, $d_{SO_3}$, which is the -SO$_3$H density per cathode total volume (mmol$_{SO_3H}$/cm$^3_{cath}$):

\[
d_{SO_3} = \frac{m_c (I / C)}{EW \cdot t_{cath}}
\]  

[3.3]

where $m_c$ is the carbon loading in the cathode (mg C/cm$^2_{cathode}$). Figure 3.6 replots the electrode proton resistivity data shown in Figure 3.4 versus $d_{SO_3}$ rather than versus I/C. As shown in Figure 3.6, $\rho_{H^+,cath}$ of electrodes prepared with 850EW and 1050EW follow the same trend line at any given RH when plotted as a function $d_{SO_3}$. The electrode proton resistivity strongly depends on the -SO$_3$H density at low values of $d_{SO_3}$, but varies only slightly at higher values of $d_{SO_3}$. While this behavior is consistent with the observation that the electrode proton resistivity becomes independent of ionomer EW in electrodes when high I/C value are used (see Figure 3.4), it does not explain why this is the case. In order to get more insight into this phenomenon, we look into the ionomer proton resistivity in films with various EW as a function of RH.
3.3.3 Proton Resistivity of Membrane Recast from Ionomer

The through-plane proton resistivity ($\rho_{i(film)}$) of membrane recast from ionomer solution is obtained by dividing the membrane resistance ($R_{i(film)}$) by its thickness. The $R_{i(film)}$ is determined at various RH levels at 80°C in H$_2$/N$_2$ cells using ac impedance by measuring the HFR, which is the sum of proton resistance of the membrane and the cell’s electronic resistances, $R_{electronic}$, which is largely due to the compression dependent contact resistance between the flow-field and the diffusion media.$^{1, 21}$ For a 50 cm$^2$ cell

---

**Figure 3.6**: Proton resistivity in electrodes made with different ionomers as a function of –SO$_3$H group density in the electrode at various RHs and at 80°C. Solid symbols represent electrodes with 1050EW ionomer, and open symbols represent electrodes with 850EW ionomer.
used in this study, a typical value of $R_{DM/FF}$ is $\sim 25 \text{ m\Omega \cdot cm}^2$ which is obtained by resistance measurements on a fuel cell without MEA (for experimental details see Ref. 3). The dependence of membrane thickness on RH and temperature was calculated by assuming that the membrane constrained by the flow-fields in the in-plane direction would only expand in the thickness direction, as was found previously.\textsuperscript{18, 19} The membrane actual thickness, $t_{\text{mem}}(\text{RH}, T)$, can be estimated by\textsuperscript{7}

\[
t_{\text{mem}}(\text{RH}, T) = t_{\text{mem,dry}} \left(1 + \frac{M_w \cdot d_{\text{mem,dry}} \cdot \lambda(T, \text{RH})}{d_w \cdot EW}\right)
\]  \hspace{1cm} [3.4]

where $t_{\text{mem,dry}}$ is the dry membrane thickness in units of cm, $M_w$ is the water molar molecular weight (g/mol), and $d_w$ is the water density (at $25^\circ C$ $d_w = 1.00 \text{ g/cm}^3$).\textsuperscript{22} The number of water molecules per sulfonic acid group, $\lambda$, as a function of temperature and RH for both EW ionomers can be calculated from the following equation for RH values of $\leq 80\%$RH (Eq. 1 in Ref. 23):

\[
\lambda(\text{RH}) = \left[1 + RH^2 \cdot 0.2352 \cdot \left(\frac{T-30}{30}\right)\right] \cdot \left(14.22 \cdot RH^3 - 18.92 \cdot RH^2 + 13.41 \cdot RH\right)
\]  \hspace{1cm} [3.5]

At fully saturated conditions ($122\%$RH), $\lambda$ is 22 at $80^\circ C$ for both EW ionomers. $d_{\text{mem,dry}}$ is the dry membrane density (g/cm$^3$), which was determined using weight measurement at room temperature ($25^\circ C$) and ambient environment (RH=50\%, $\lambda$\textsuperscript{24}), and was calculated by Equation 3.6 (same as Equation B.5). The detailed derivation of this formula is described in the Appendix B.
\[ d_{\text{mem,dry}} = \frac{EW \cdot d_{\text{mem,wet}}}{(EW + \lambda M_w) - \frac{M_w \lambda d_{\text{mem,wet}}}{d_w}} \]  

where \( d_{\text{mem,wet}} \) is the density of the wet membrane at certain temperature and RH, which could be obtained by dividing mass of the wet membrane \( (m_{\text{mem,wet}}) \) by its volume \( (V_{\text{mem,wet}}) \). The volume was obtained by measuring the membrane sheet width and length using calipers and the membrane thickness of 19±1 µm was obtained using a thickness gauge and was verified by SEM cross-section measurements (see Figure 3.7). At 25°C and 50%RH, based on the measured values of \( m_{\text{mem,wet}} \) and \( V_{\text{mem,wet}} \), the obtained densities of the dry membranes are 2.10 and 2.14 g/cm\(^3\) for the 850EW (DE2029\(^\circledR\)) and the 1050EW (DE2021\(^\circledR\)) ionomers, respectively. The latter value is reasonably consistent with the published values for 1050EW Nafion\(^\circledR\) membranes of 2.08\(^{25}\) and 2.11 g/cm\(^3\) (obtained from Equation 3.6 and using \( \lambda \approx 4 \) at 50% RH and room temperature). There are no published values for 850EW ionomer (DE2029\(^\circledR\)). Figure 3.8 shows the dependence of \( \rho_{i(\text{film})} \) on RH at 80°C for membranes recast from both ionomer solutions. It is not surprising that the \( \rho_{i(\text{film})} \) of the 850EW ionomer recast membrane \( \rho_{i(\text{film}),850EW} \) is lower than the \( \rho_{i(\text{film}),1050EW} \) at all RH levels. The resistivity ratio of these two recast membranes (\( \rho_{i(\text{film}),850EW} / \rho_{i(\text{film}),1050EW} \)) is also shown in Figure 3.8 (\( \Delta \)) and for 25 to 100% RH a constant ratio of ~0.6 is found.
Figure 3.7: Thickness of recast membrane (a) from 850EW ionomer and (b) with 1050EW ionomer under SEM observation. SEM images were taken under in-lens secondary electron under 2.0kV energy mode.
Figure 3.8: Recast membrane resistivity as a function of RH (20% to 100%) at 80°C determined by subtracting $R_{DM/FF}$ from HFR measured by AC impedance. Data points (Δ) represent the proton resistivity ratio of these two types of recast membranes.

The measured ratio of the $\rho_{H^+,cat}$ values obtained for the low EW electrodes over that of the high EW electrodes is plotted in Figure 3.9. Dashed lines represent the experimental data based on the data shown in Figure 3.4. As shown in Figure 3.9, when the I/C-ratio is 0.6 and 0.4 at subsaturated conditions, the proton resistivity ratios of the different EW electrodes (two lower dashed lines in Figure 3.9) is essentially the same as the ratio of $(\rho_{i(film),850EW}/\rho_{i(film),1050EW})$ of the ionomer films (Δ in Figure 3.8). On the other hand, for I/C-ratios of 0.8 and 1.0, there is almost no effect of the ionomer EW on electrode proton resistivity (i.e., a ratio of nearly one in Figure 3.9). It implies that once the ionomer content reaches a certain level, increased ionomer conductivity (i.e., going
from high to low EW ionomer) does not significantly increase the proton conduction in the electrode. In addition, it is also shown that at fully humidified condition, the proton resistivity ratio of the two types of electrodes is essentially independent of I/C-ratios, which is different from the recast membrane resistivity ratio, indicating the possibility of alternative proton conduction path. This alternative path can be formed on the surface of the ionomer thin layer and consists of -SO$_3$H groups, which upon exposure to water can form a continuous path of aqueous thin layer. To further understand this observation, the proton conduction in ultra thin ionomer film is discussed in the next section.

**Figure 3.9:** Ratio of the cathode proton resistivities of 850EW electrodes over the 1050EW electrodes. Error bars represent the maximum and minimum deviation from the average ratio at each condition.
3.3.4 Proton Conduction in Ultra Thin Ionomer Layer

The chemical and physical structure of ultra thin ionomers is an open question of fundamental importance. The aqueous domains in bulk ionomer are claimed to be on the order of several nanometers. Once the thickness of the ultra thin layer approaches 1-3nm, it is possible that the ionomer undergoes phase transformation where its hydrophilic sulfonic acid groups go to the surfaces of the ultra thin layer, establishing an aqueous layer responsible for much of the proton conduction.

3.3.4.1 Is It Possible to Form a Continuous Thin Water Layer?

Direct observation or measurement of the configuration of ionomer on the carbon supported catalyst is very difficult, if not impossible. Assuming homogeneous film formation on the carbon supported catalyst, the film thickness ($\delta_i$) can be estimated by

$$\delta_i = \frac{1}{(I/C)d_{\text{mem,dry}}A}$$

[3.7a]

where $A$, the catalyst surface area, could be represented by its N$_2$ BET area ($A_{\text{BET}}$) or by its geometric area ($A_{\text{geo}}$). For Pt/Vulcan catalyst, by ignoring the surface area of Pt and using the total BET surface area of Vulcan (~250 m$^2$/g), the ionomer film thickness can be estimated by

$$\delta_{i,\text{BET}} = \frac{1}{(I/C)d_{\text{mem,dry}}A_{\text{BET}}}$$

[3.7b]

At I/C=1 with $d_{\text{mem,dry}}$ of ~2g/cm$^3$, the $\delta_{i,\text{BET}}=2$nm.

If the carbon is assumed to be spherical particles with an averaged diameter ($D$) of 40nm, the geometric area per gram of carbon is given by
\[ A_{geo} = \frac{1}{\rho_C} \frac{D}{6} = \frac{1/(2g/cm^3)}{40nm/6} = 75m^2/g \]  

where \( \rho_C \) is the carbon density \((g/cm^3)\). The ionomer thickness is thus given by

\[ \delta_{i,geo} = \frac{1}{1 \times 2g/cm^3 \times 75m^2/g} = 6.7nm \]

Due to the fact that not all the BET area is accessible to the ionomer and the carbon is actually very porous, it is reasonable to estimate an averaged ionomer thickness of 3-4 nm on the catalyst surface. Based on the this estimation, the well-known Gierke Cluster Network Model\(^{26} \) for the membrane, as shown in Figure 3.10, might not be applicable for ultra thin films. In the Gierke model, the clusters are formed by inverted-micelles assembled by the -SO\(_3\)H-ended side chains with a size of \(\sim\)4nm, and connected with neighbors by a \(\sim\)1 nm channel or pore in size. However, under the situation that only 3-4 nm thick ionomer film formed on the carbon surface, the inverted-micelles are not favored to form. There are two hypothesized configurations for the ultra thin layer of ionomer on a carbon support, as illustrated in Figure 3.11. On one hand, Figure 3.11a represents the ionomer backbone absorbed on carbon, while the SO\(_3\)H-ended side chains are directed towards the void or gas phase. This configuration might require great activation energy in order to extend the backbone, and the adsorption between the carbon and ionomer needs to be strong in order to maintain this configuration. Figure 3.11b, on the other hand, demonstrates a micelle like configuration also assembled by the SO\(_3\)H-ended side chains. Comparing to the first configuration, this one might be energetically easier to form. Moreover, during cell operation, the electrode void is full of water vapor, favoring this configuration. Nevertheless, no experimental evidence is available to prove...
one or the other, as this remains an open question.

Figure 3.10: Gierke Cluster Network Model.26

Figure 3.11: Ionomer configuration in the electrode. Symbol ○ represents Pt nanoparticle. (a): ionomer backbone absorbed on catalyst and -SO₃H ended side chain towards water vapor phase, (b): ionomer forms micelles and absorbed on catalyst.

3.3.4.2 Estimation of Distance between Neighboring SO₃H Groups

The number of SO₃H groups in dry ionomer, \( n_{SO_3H} \) (cm⁻³), can be estimated by

\[
n_{SO_3H} = \frac{N_A}{EW / d_{\text{mem,dry}}} \tag{3.8}
\]

where \( N_A = 6.02 \times 10^{23} \text{mol}^{-1} \) is the Avogadro’s number. For 850EW ionomer, \( n_{SO_3H} = 1.35 \times 10^{21} \text{cm}^{-3} \), and for 1050EW ionomer, \( n_{SO_3H} = 1.16 \times 10^{21} \text{cm}^{-3} \). The volume of each unit having one -SO₃H group is 7.41×10⁻²²cm³ and 8.62×10⁻²²cm³ for 850EW and
1050EW, respectively. Therefore, the distance \( r \) between neighboring SO\(_3\)H for both ionomers is \( \sim 1\, \text{nm} \), as shown in Figure 3.12a. This should be the maximum spacing between two neighboring SO\(_3\)H groups on an exposed surface. Based on the ionomer thickness calculation in Section 3.3.4.1, when I/C=0.4 the coverage is low and amounts to a monolayer. If the water uptaken by each SO\(_3\)H group are uniformly distributed on the surface of the ionomer layer, the thickness of the water film can be calculated by

\[
\delta_{\text{H}_2\text{O}} = \frac{\lambda/ N_A \cdot 18}{r^2}
\]  

[3.9]

At \( \lambda=4 \), \( \delta_{\text{H}_2\text{O}}=1\,\text{Å} \), which is smaller than a water molecule size of \( \sim 0.3\,\text{nm} \). Therefore there is no continuous water film formed on the either ionomer layer surface. At this I/C-ratio, water could form a continuous film by using ionomer with \( \sim 500\text{EW} \) or under fully humidified condition, as shown in Figures 3.12 b and c, respectively. At the same operating condition, by increasing the I/C by a factor 2, \( \delta_{\text{H}_2\text{O}} \) becomes 4Å, so it is very possible to form a monolayer water film on the ionomer layer surface, providing a proton transport path. This is demonstrated by Figure 3.12d

The above analysis can possibly be used to explain the observation in Figure 3.9 by a proton transport mechanism as indicated in Figure 3.12. Figure 3.12a represents the electrode with high EW ionomer at low I/C (i.e., I/C\( \leq 0.6 \)) and at a subsaturated condition, i.e., RH=50% \( \mathcal{(4)} \), where the adsorbed water molecules have not yet formed a continuous path for the proton transportation. The proton conduction in the electrode is determined by the intrinsic ionomer proton conductivity, which depends strongly on the ionomer EW, i.e., lower EW ionomer exhibits lower proton resistivity due to the presence of more –SO\(_3\) groups facilitating the H\(^+\) conduction, as shown in Figure 3.12b. Note that
in this work, neither ionomer could represent this case. When RH or $\lambda$ reaches a certain level, the water itself can form a network to facilitate the proton conduction in addition to the existing ionomer network even at low I/C (i.e., I/C $\leq 0.6$), as shown in Figure 3.12c, which explains why at fully humidified conditions the $\rho_{H^+,cath}$ ratios of these two types of electrodes are around 1. If the ionomer content is increased to or above a certain level (i.e., I/C $\geq 0.8$, represented by adding another ionomer chain), as demonstrated in Figure 3.12d (for high EW ionomer), there are enough $-$SO$_3$ groups for both electrodes to form a H$^+$ conduction path even at lower RH or $\lambda$ so that the RH has little effect on the proton transport in the electrode, which explains that when I/C $\geq 0.8$ almost no difference between the two electrodes with different EW ionomers is observed from the electrode proton resistivity point of view. It should be noted that Figure 3.12 does not represent the actual ionomer configuration in the electrode, and it only shows the interaction among the $-$SO$_3$H groups with the absorbed water.

There is another possibility that the simple exposure of the surface does not produce enough $-$SO$_3$H groups to form a continuous water layer. Therefore it is possible that the Gierke clusters undergo phase transition, where most $-$SO$_3$H groups are directed towards the surface where a thin layer of aqueous solution is formed. For 1050 EW, for example, 1nm thin layer contains $1.16 \times 10^{14}$ SO$_3$H/cm$^2$ in a 1cm$^2 \times$1nm volume knowing that $n_{SO_3H} = 1.16 \times 10^{21}$ SO$_3$H/cm$^3$. Thus this distance between neighboring $-$SO$_3$H groups is $\sim$1nm, again insufficient for a continuous layer. It is quite possible that a network of water is established instead on the surface. Again, these are only hypotheses, as there’s no direct evidence to prove one or the other, so this remains an open question.
Figure 3.12: Schematics (\(\text{●}\) represents a \(\text{H}_3\text{O}^+\), \(\text{ ○}\) represents a \(\text{H}_2\text{O}\) molecule, and \(\bigcirc\) represents a \(-\text{SO}_3^-\) group) of proton transport path in the electrode with: (a) high EW ionomer and low I/C-ratio in the electrode at 50%RH (\(\lambda\approx4\)); (b) low EW ionomer and low I/C-ratio in the electrode at 50%RH; (c) low I/C-ratio in the electrode at RH\(\geq100\%\) (\(\lambda\geq8\) at 80 °C); (d) high I/C-ratio in the electrode at 50%RH (\(\lambda\approx4\)).

3.3.5 Effect of Ionomer EW on \(\text{H}_2/\text{O}_2\) Cell Performance

In the following section, we use the measured \(R_{\text{H}^+,\text{cath}}\) of various electrodes to compare the electrode proton resistance-corrected cell performance \((E_{iR-free}, \text{ see Equation}\)
between electrodes with lower and higher EW ionomers, using a 50%wt. Pt/V catalyst at a nominal loading of 0.4 mgPt/cm². It is expected that electrodes with lower EW ionomer at the same I/C should show higher cell voltage under the same conditions before the electrode proton resistance correction. After the electrode proton resistance correction, they should show the same performance provided that each MEA has the same nominal Pt-loading of 0.4mgPt/cm²\textsubscript{MEA}.

The cell voltages ($E_{\text{cell}}$) of electrodes with 1050EW and 850EW ionomers at 0.1A/cm² in H₂/O₂ at 122%, 75%, 50% and 35%RH are shown in Figure 3.13.
Figure 3.13: Dependence of the cell voltage at 0.1A/cm² in H₂/O₂ at 80°C on the electrodes’ I/C-ratio at 122%, 75%, 50%, and 35%RH. Solid symbols represent electrodes with 1050EW ionomer, and hollow symbols represent electrodes with 850EW ionomer.

As expected from the above discussion, cell performance does not benefit from lowering the ionomer EW at I/C-ratio of 0.8 or higher (compare the open vs. solid symbols at high I/C-ratios in Figure 3.13). While at I/C-ratio of 0.6 or lower, the higher conductivity of the low EW ionomer electrodes does result in higher cell voltages,
especially at dry operating conditions. It is essentially due to increased $d_{SO_3}$ in the electrode at the same I/C. For example, at 35% RH the $E_{cell}$ of electrodes with 850EW ionomer is higher than of electrodes with 1050EW ionomer by $\sim$30mV at I/C of 0.4, and $\sim$20mV at I/C of 0.6. It is also noticed that at 122%RH, the low EW ionomer electrode’s performance is only higher than the high EW ionomer electrode at I/C-ratio of 0.4 by $\sim$10mV. At I/C=1.0 and 122%RH, cell voltage drops dramatically ($\sim$40mV) for electrodes with the low EW ionomer compared to the high EW ionomer electrodes at the same I/C. This is likely due to the increased $d_{SO_3}$ in the electrode which holds more water and thus causes flooding. This problem disappears only when I/C-ratio is decreased to 0.4, where the volume fraction of ionomer (or the $d_{SO_3}$) in the electrode is very small.

The HFR and electrode proton resistance corrected voltage can be expressed by\textsuperscript{6,7}

\[ E_{iR-free} = E_{rev} - \eta_{ORR} = E_{cell} + i \cdot HFR + i \left( \frac{R_{H+,cath}}{3 + \zeta} \right) \]  \[3.10\]

where $\zeta$ is a correction factor defined in Ref. 1. The first two terms ($E_{cell} + i \cdot HFR$) in the right hand side of Equation 3.10 is HFR corrected voltage, $E_{HFR-free}$. The dependence of $E_{HFR-free}$ and $E_{iR-free}$ on I/C-ratio at four RH levels is plotted in Figures 3.14 and 3.15, respectively. As indicated in Equation 3.10, $E_{HFR-free}$ should be dependent on I/C-ratio because of the dependence of $\rho_{H+,cath}$ and $\zeta$ on the electrode’s I/C-ratio, while $E_{iR-free}$ should be independent of the I/C-ratio since neither $E_{rev}$ nor $\eta_{ORR}$ is a function of I/C. It is shown in Figure 3.14 that with HFR correction, the voltages still vary with I/C-ratio from 800mV to 900 mV. Only when the losses caused by proton conduction in the electrode are included, the voltages become independent of I/C-ratio with the exception of the
electrodes with 850EW ionomers at I/C=1, as shown in Figure 3.15. The poor performance of these electrodes at I/C=1 was caused by flooding as previously discussed, they are out of discussion. It is obvious that all of the $E_{ir-free}$ studied in this work lie in a band of 887±13 mV as defined by two dashed lines in Figure 3.15. This is consistent with the results reported previously.$^{6,7}$

**Figure 3.14:** Dependence of HFR-corrected cell voltages at 0.1A/cm$^2$ in H$_2$/O$_2$ at 80°C on electrode’s I/C-ratio at 122%, 75%, 50%, and 35%RH. Each data point represents an independent measurement on a different MEA. Cathode platinum loadings are 0.4 mgPt/cm$^2$. 
3.4 SUMMARY

In summary, continuing our previous study to determine the proton resistance of a cathode using AC impedance in an H₂/N₂-fed cell, we were able to validate our previous conclusion that the electrode proton resistivity is an intrinsic property of the PEMFC electrode. The proton resistivity for uniform electrodes is independent of the electrode
thickness and the carbon-supported Pt %wt, provided that the same I/C and carbon type are maintained. The proton resistivity of the cathodes has strong dependence on the ionomer EW at lower I/C-ratio. It indicates that the electrode proton resistivity is essentially a function of the density of -SO$_3$H groups, $d_{SO_3H}$ at subsaturated conditions, while at fully humidified conditions the electrode resistivity becomes independent of the $d_{SO_3H}$. This finding provides helpful information for electrode design, indicating that $d_{SO_3H}$ is likely a key parameter to control the necessary ionomer content in the electrode. When the ionomer layer is ultra thin (~1nm), the mechanism for proton conduction might change due to chemical and physical transformation. The surface density of -SO$_3$H groups may reach a level such that a thin water layer is formed on the face of the thin ionomer layer to facilitate proton conduction there. The measured $\rho_{H^+,cath}$ was successfully used to predict the influence of the cathode’s proton resistivity on the MEA performance. Electrodes with EW850 ionomer exhibit higher cell voltage than electrodes with EW1050 ionomer at low I/C-ratios and low RH levels due to increased -SO$_3$H density in the low EW ionomer electrode. However, at fully humidified condition, worse performance is observed except at I/C-ratio of 0.4. HFR and electrode’s proton resistance-corrected voltage are independent of I/C-ratio at all RH levels regardless of the ionomer conductivity.

SYMBOLS

$A_{BET}$ carbon N$_2$ BET area, m$^2$/g
$A_{geo}$ carbon geometric area, m$^2$/g
$C_{cath}$ cathode capacitance, F/cm$^2$ MEA
$d_c$ density of carbon support, g/cm³

$d_{mem,dry}$ density of dry recast membrane, g/cm³

$d_{mem,wet}$ density of wet recast membrane, g/cm³

$d_{SO3}$ density of $-\text{SO}_3\text{H}$ group per electrode volume, mmol/cm³_{electrode}

$d_w$ density of water, g/cm³

$E_{cell}$ observed cell voltage, V

$E_{HFR-free}$ observed cell voltage corrected by high frequency resistance, V

$E_{iR-free}$ iR-free cell voltage, observed cell voltage plus corrections from proton resistance in the cathode and high frequency resistance, V

$E_{rev}$ reversible cell potential (function of $T$, $p_{H_2}$, $p_{O_2}$, RH), V

$f$ frequency, Hz

$f_t$ factor for electrode thickness calculation, $28\pm2\mu\text{m}/(\text{mgC/cm}^2_{electrode})$

$i$ current density, A/cm²

$m_C$ carbon loading in the electrode, mg/cm²_{MEA}

$m_{mem,dry}$ mass of the dry recast membrane, g

$m_{mem,wet}$ mass of the dry recast membrane plus absorbed water, g

$m_w$ mass of the absorbed water in recast membrane, g

$M_w$ water molecular weight, g/mol

$N_A$ Avogadro’s number, $6.02\times10^{23}\text{mol}^{-1}$

$r$ distance between neighboring $-\text{SO}_3\text{H}$ groups, nm

$R_{DM/FF}$ compression-dependent contact resistance between the flow field and diffusion media, Ω⋅cm²

$R_{electronic}$ electronic resistance of the cell, Ω⋅cm²

$R_{H^+,cath}$ proton resistance in the cathode, Ω⋅cm²

$R_{i(film)}$ proton resistance of recast membrane or ionomers in film form, Ω⋅cm²

$l_{cath}$ cathode thickness, cm

$V_{mem,wet}$ volume of recast membrane, cm³

Greek

$\delta_{i,BET}$ ionomer thickness estimated by carbon N₂ BET area, nm
δ_{i,geo} \quad \text{ionomer thickness estimated by carbon geometric area, nm}
δ_{H_2O} \quad \text{water film thickness estimated by carbon geometric area, nm}
ε_i \quad \text{ionomer volume fraction in cathode}
η_{ORR} \quad \text{overpotential of the ORR, V}
ρ_{H^+,an} \quad \text{proton resistivity in the anode, Ω\cdot cm}
ρ_{H^+,cath} \quad \text{proton resistivity in the cathode, Ω\cdot cm}
ρ_{H^+,electrode} \quad \text{proton resistivity in the electrode, Ω\cdot cm}
ρ_{(film)} \quad \text{proton resistivity of recast membrane or ionomers in film form, Ω\cdot cm}
τ_{ε_i} \quad \text{tortuosity of ionomer (proton conduction) in the electrode (function of ionomer volume fraction)}
ζ \quad \text{correction factor for reduced cathode proton transport length to membrane}

REFERENCES


Chapter 4

Model for Proton Conduction in PEM Fuel Cell Cathodes

4.1 INTRODUCTION

The electrodes in a Proton Exchange Membrane (PEM) fuel cell consist of carbon-supported Pt catalyst coated with a thin layer of ionomer. Oxygen reduction reaction (ORR) occurs at the cathode, where protons reach the catalyst sites via the thin ionomer layer. The cathode proton resistance ($R_{H^+, \text{cath.}}$) through the thickness of the cathode can generate significant voltage losses, especially under dry conditions. The $R_{H^+, \text{cath.}}$ in a cathode with various ionomer/carbon mass ratios, $(I/C)_m$, has been previously measured in a H$_2$/N$_2$ cell using AC impedance under various operating conditions. The effects of $(I/C)_m$, equivalent weight (EW) of ionomer and relative humidity (RH) have been systematically studied in Chapters 2 and 3. However, some open questions still exist, such as the chemical and physical configurations of the ionomer in the electrode, and the difference in proton conductivity for ionomer in membrane (~10μm thick) and thin film in nanometer scale. Because the carbon particles are porous, and the pores are ranging from nanometers to micrometers, it is usually believed that some portion of the ionomer is absorbed into the pores, which would not contribute to the proton conduction, so the effective I/C is smaller than what was added while making the ink. It should be noted that the pores inside of the particles are thought to be interstitial and thus different from normally envisioned. Whether or not and how much ionomer is absorbed into the pores is also uncertain. Another uncertainty is the thickness of the ionomer film. In Chapter 3, a
value based on catalyst N$_2$ BET area was estimated, but it is also not accurate because not all BET area is accessible to the ionomer. In this chapter, a mathematical model, a thin shell model, is presented for the proton conduction as a function of the volumetric fraction of the ionomer in the cathode. The model assumes uniform distribution of the ionomer over the carbon particles. It is further assumed that the thickness of the electrode is determined by the amount of carbon per projected unit area. By fitting the model predictions to the data obtained in previous chapters, the effects of carbon roughness and its porosity are discussed based on the model and data comparison. One of the main conclusions of this study is that the ionomer-to-carbon volumetric ratio, (I/C)$_v$, is a fundamental parameter for understanding the correlation between the proton resistivity in the electrode and the membrane. A major difference between the (I/C)$_m$ and (I/C)$_v$ is that the swelling of the ionomer is taken into account under various RH conditions. It should be noted that (I/C)$_v$ is related to the previously defined term in Chapter 2, ionomer volume fraction, $\varepsilon_i$, as described by Equation 2.12. The (I/C)$_v$ is equal to the ratio of $\varepsilon_i$ over the carbon volume fraction ($\varepsilon_C$), which is essentially kept constant and independent of (I/C)$_m$, therefore the (I/C)$_v$ is directly proportional to the ionomer volume fraction.

### 4.2 DESCRIPTION OF THIN SHELL MODEL

#### 4.2.1 Ionomer-to-carbon Volumetric Ratio

The proton resistivity in the cathode can be theoretically calculated by constructing a model in which the carbon particles are assumed to be spheres with a radius of $a$. The spheres are packed together and covered by a thin layer of ionomer with a thickness of $\delta$,
as illustrated in Figure 4.1. Here, the carbon spheres are cubically packed, the volume fraction of carbon particles are ~50% of the total volume for perfectly packed electrode.

![Figure 4.1: Theoretical model: carbon spheres covered by ionomer.](image)

The volumetric ratio of ionomer to carbon \((I/C)_v\) can be calculated by

\[
(I/C)_v = \frac{\frac{4\pi}{3}[(a + \delta)^3 - a^3]}{\frac{4\pi}{3}a^3} = (1 + \frac{\delta}{a})^3 - 1
\]  

[4.1]

For the case \(\delta < a\):

\[
(I/C)_v = \frac{\frac{4\pi a^2 \delta}{4\pi \frac{3}{a^3}}} = \frac{3\delta}{a}
\]  

[4.2]

The volumetric ratio can be obtained from the experimentally prepared \((I/C)_m\) by

\[
(I/C)_v = (I/C)_m \frac{d_e}{d_{mem,wet}}(1 + \frac{M_w \lambda}{EW})
\]  

[4.3]
where \( d_c \) (2 g/cm\(^3\)) is the densities of the carbon, \( M_w \) is the water molecular weight (18 g/mol), and EW is the equivalent weight of the ionomer. \( d_{\text{mem, wet}} \), the wet ionomer (i.e. membrane), can be estimated by

\[
d_{\text{mem, wet}} = \frac{EW + \lambda M_w}{d_{\text{mem, dry}} M_w \lambda + \frac{EW}{d_w}} \tag{4.4}
\]

where \( d_{\text{mem, dry}} \) is the dry ionomer density, which was determined in Chapter 3 as 2.1 g/cm\(^3\) for 850 EW ionomer and 2.14 g/cm\(^3\) for 1050 EW ionomer. The number of water molecules per sulfonic acid group, \( \lambda \), as a function of temperature and RH for both EW ionomers can be calculated from the following equation for RH values of \( \leq 80\% \text{RH} \) (Eq. 1 in Ref. 5):

\[
\lambda(RH) = \left[ 1 + RH^2 \cdot 0.2352 \cdot \left( \frac{T - 30}{30} \right) \right] \cdot \left( 14.22 \cdot RH^3 - 18.92 \cdot RH^2 + 13.41 \cdot RH \right) \tag{4.5}
\]

At fully saturated conditions (122\%RH), \( \lambda \) is 22 at 80°C for both EW ionomers.

4.2.2 Proton Resistivity in the Cathode: Thin Shell Model

The resistance in the thin layer of the ionomer can be calculated along the spherical coordinate \( \theta \), as shown in Figure 4.2.
Figure 4.2: Theoretical model: Integration over the ionomer shell. Arrows represent the current direction.

To ensure electron conduction through the electrode, adjacent carbon support particles have to be in contact. In Figure 4.2, $\theta_o$ is the angle from the point of contact to the neighboring sphere where there is no current goes through.

$$\cos(\theta_o) = \frac{a}{a + \delta / 2}$$  \[4.6\]

Protons transport in the thin film over the spherical particle from $\theta_o$ to $\pi - \theta_o$. The resistance can be calculated by

$$dR_{H^+,cath} = \frac{\rho_{i(\text{film})}}{2\pi(a + \delta / 2)\sin(\theta)\delta} \cdot \frac{d\theta}{\sin(\theta)} = \frac{\rho_{i(\text{film})}}{2\pi\delta} \cdot \frac{d\theta}{\sin(\theta)}$$  \[4.7\]

$$R_{H^+,cath} = \frac{\rho_{i(\text{film})}}{2\pi\delta} \cdot \int_{\theta_o}^{\pi - \theta_o} \frac{d\theta}{\sin(\theta)} = \frac{\rho_{i(\text{film})}}{2\pi\delta} \cdot \int_{\theta_o}^{\pi / 2} \frac{d\theta}{\sin(\theta)} = \frac{\rho_{i(\text{film})}}{2\pi\delta} \cdot \left\{ -\frac{1}{2} \ln \left[ \frac{1 + \cos(\theta)}{1 - \cos(\theta)} \right] \right\}_{\theta_o}^{\pi / 2}$$

$$= \frac{\rho_{i(\text{film})}}{2\pi\delta} \cdot \ln \left[ \frac{1 + \cos(\theta_o)}{1 - \cos(\theta_o)} \right]$$  \[4.8\]
where $\rho_{\text{film}}$ is the ionomer proton resistivity. Substituting Equation 4.6 into Equation 4.8, one gets

$$R_{H^+,\text{cath}} = \frac{\rho_{\text{film}}}{2\pi\delta} \cdot \ln\left(1 + \frac{4a}{\delta}\right) \quad [4.9]$$

The proton resistance can also be represented by defining the average medium resistivity for the sphere

$$R_{H^+,\text{cath}} = \rho_{am} \cdot \frac{2a}{(2a)^2} = \rho_{am} \cdot \frac{1}{2a} \quad [4.10]$$

where $\rho_{am}$ is the average medium resistivity of the cathode layer of cross sectional area $4a^2$ and a length of $2a$ (neglecting the ionomer thickness). $\rho_{am}$ is equivalent to the $\rho_{H^+,\text{cath}}$ measured in previous section. Later on, the $\rho_{am}$ is replaced with the $\rho_{H^+,\text{cath}}$ whenever it is applied. Equating the two previous equations gives

$$\rho_{H^+,\text{cath}} = \frac{\rho_{\text{film}}}{\pi} \cdot \frac{(a/\delta) \ln[1 + 4(a/\delta)]}{(I/C)_v} \quad [4.11]$$

Since the $(\delta /a)$ can be expressed in term of $(I/C)_v$, see Equation 4.2, one obtains

$$\frac{\rho_{H^+,\text{cath}}}{\rho_{\text{film}}} = \frac{3}{\pi(I/C)_v} \cdot \ln[1 + \frac{12}{(I/C)_v}] \quad [4.12]$$

This result indicates that the normalized cathode proton resistivity depends only on the $(I/C)_v$. It must be noted that this model does not consider the roughness factor of the carbon support nor its porosity, so the effective ratio might be different for comparisons between electrodes with different carbon-support catalysts at the same $(I/C)_v$, given the
same ionomer in the cathode. This correlation is later compared with the experimental data.

4.3 EXPERIMENTAL

Electrode Proton Resistance

The data used to verify the theoretical model have appeared in Chapter 2 and 3. The essentially relevant experimental conditions are repeated here. MEAs with 50 cm² active area were fabricated in-house by hot pressing electrode decals onto 25-µm thick Nafion® membranes (DuPont, USA) with 1050EW. The ionomer used in the electrodes had the EW of 1050 or 850. Anode Pt loadings were ~0.4 mgPt/cm² and all anodes had an I/C-ratio of ~0.9. The (I/C)m of the different cathodes ranged from 0.4 to 1, using a ~50% Pt/Vulcan catalyst (Tanaka, Japan) at a nominal loading of ~0.4 mgPt/cm², whereby the precise Pt loading was determined by weight measurements of the decal before and after lamination of the electrode. The thickness of electrodes based on Vulcan or Ketjenblack supports and for I/C-ratios of <2 only depends on the carbon loading of the electrode, so that the electrode thickness can be calculated from the carbon loading multiplied by 28 µm/(mgC/cm² electrode). The detailed information about these electrodes has appeared in Tables 2.1 and 3.3.

The proton resistance in the cathode was measured by AC impedance spectra of H₂/N₂ cell where the N₂-fed working electrode (“cathode”) was potentiostated at +0.2 V vs. the H₂-fed counter/reference electrode (“anode”). All of the experiments were conducted at 80°C at four different inlet/outlet RH-values. The data analysis followed a less complex equivalent circuit in which the nonlinear charge transfer resistance vanishes.
This corresponds to a H$_2$-fed anode (reference/counter electrode) and a N$_2$-fed cathode (working electrode).

**Resistivity of Recast Membranes**

The membranes used for determining the ionomer bulk resistivity were prepared by casting the corresponding as-received ionomer solution on a glass plate at room temperature and dried overnight. All of the cast membranes were then annealed at 130°C for 4 hrs before assembling with electrodes. Both membranes had a thickness of ~20 μm at room temperature and ambient environment, and they were incorporated into MEAs for membrane conductivity characterization using AC impedance. It should be noted that when the membrane resistivity is applied, the increase of membrane thickness due to water uptake and swelling is considered (assuming swelling only in thickness direction due to x/y constraint$^7, 8$). The anodes were the same for the $R_{H^+, \text{cath}}$ measurements, and the cathodes were fabricated using ~50%wt. Pt/V and DE2021® 1050EW ionomer with an I/C of 0.8/1 at ~0.4 mgPt/cm$^2$ Pt loading.

### 4.4 RESULTS AND DISCUSSION

#### 4.4.1 Experimental Data

Figure 4.3 shows the cathode proton resistivity as a function of (I/C)$_m$ for both EW ionomers at various RHs. The ionomer resistivities for each ionomer at various RHs are shown in Figure 4.4. The normalized cathode proton resistivity is obtained by dividing $\rho_{H^+, \text{cath}}$ by $\rho_{i(\text{film})}$, and the ratio of these two can be obtained at each condition. If the ratio is plotted versus (I/C)$_m$, as shown in Figure 4.5, normalizing each curve by its
corresponding ionomer resistivity (membrane resistivity) does not result in a single curve, indicating that the effect of RH has to be considered. Normalizing each curve by the ionomer resistivity and converting $(I/C)_m$ to $(I/C)_v$ results in a single curve, as presented by Figure 4.6. This merging of the various data into a reasonably good universal curve indicates that the proton conductivity is indeed an intrinsic property of the ionomer to carbon volume ratio and ionomer swelling must be considered. Some data scattering can be observed in the high $(I/C)_v$ for fully humidified 850EW electrodes. A possible reason is that at this condition, the low resistance becomes comparable to the cell’s contact resistance, introducing an unavoidable error.

![Figure 4.3: Dependence of the electrode proton resistivity on the cathode ionomer EW at 122%, 75%, 50%, and 35%RH in H₂/N₂ at 80°C. Dashed lines indicated the resistivity obtained for 850 EW electrodes while solid lines represent the resistivity obtained for 1050 EW electrodes. Data points represent independent measurements on different MEAs. This figure is the same as Figure 3.4.](image-url)
Figure 4.4: Recast membrane resistivity as a function of RH (20% to 100%) at 80°C determined by subtracting $R_{\text{DM}/\text{FF}}$ from HFR measured by AC impedance. This figure is the same as Figure 3.8.

Figure 4.5: Dependence of normalized resistivity on mass ratio $(I/C)_m$. Note that the data do not converge into a single universal curve.
4.4.2 Comparison of Model to Experimental Data

Figure 4.7 shows the same data plotted vs. the (I/C)_v in Figure 4.6 while incorporating the thin shell model prediction, as illustrated by the solid curve. The model successfully predicts the data trend. However, the predicted values are much lower than the experimental data, indicating that the effective (I/C) is less than what added during electrode preparation. As mentioned before, the carbon support material is highly porous and rough, while the model does not take these two factors into account. To figure out the effect of each factor, some modifications are made to the thin shell model as presented by Equation 4.12.
If a roughness factor ($rf$) is considered, the ionomer thickness should be thinner than what is calculated based on smooth carbon sphere, so the Equation 4.2 becomes

$$\frac{\delta}{a} = \frac{(I/C)_v}{3(rf)}$$  \hspace{1cm} [4.13a]

Equation 4.12 is subsequently changed to

$$\frac{\rho_{H^+,\text{cath}}}{\rho_{i,\text{film}}} = \frac{3(rf)}{\pi(I/C)_v} \ln[1 + \frac{12(rf)}{(I/C)_v}]$$  \hspace{1cm} [4.13b]
This is presented by the dotted curve using $rf=1.6$ in Figure 4.7. The model curve gets closer to the data at the mid I/C range, while at the low I/C, the difference is still about an order magnitude. This implies the other possibility that some portion of ionomer was absorbed into the pores while making the electrode. If only a portion of ionomer contributes to the proton conduction, the ionomer thickness also decreases. Equation 4.2 becomes

$$\frac{\delta}{a} = \frac{(I/C)_{v} - (I/C)_{ab}}{3}$$

[4.14a]

where $(I/C)_{ab}$ is the portion of ionomer absorbed into pores referenced to the carbon volume. Consequently, Equation 4.12 can be rewritten as

$$\frac{\rho_{H^{+},cath}}{\rho_{i,film}} = \frac{3}{\pi[(I/C)_{v} - (I/C)_{ab}] \ln[1 + \frac{12}{(I/C)_{v} - (I/C)_{ab}}]}$$

[4.14b]

The above equation is presented by the dashed curve, as shown in Figure 4.7 with the $(I/C)_{ab}=0.3$. This modification brings the model curve much closer to the data, especially at the low I/C. If these two effects are combined, the model is expressed by

$$\frac{\rho_{H^{+},cath}}{\rho_{i,film}} = \frac{3rf}{\pi[(I/C)_{v} - (I/C)_{ab}] \ln[1 + \frac{12rf}{(I/C)_{v} - (I/C)_{ab}}]}$$

[4.15]

A dot-dashed curve representing this equation is presented also in Figure 4.7 with $rf=1.6$ and $(I/C)_{ab}=0.3$. This model fits the data very well at most I/C, though it still cannot match the data points at fully humidified 122%RH condition for 850EW ionomer electrodes. The possible reason has been stated in the previous section. It should be
mentioned that \((I/C)_{ab}\) does not represent the porosity of this carbon material because some pores are too small for the ionomer to be absorbed inside.

In all, the agreement between the model and data validates the conclusion that the medium resistivity depends on the volumetric \((I/C)_v\) ratio and is independent of the radius of the carbon particles, but it does depend on the roughness and porosity of the carbon particles. Note that this model assumes the carbon as spheres and being cubically packed. Improvement can be obtained if the packing pattern is changed as well as the shape of the carbon particles and their tendency to agglomerate.

### 4.5 SUMMARY

A model for proton conductance in the cathode of a PEM fuel cell has been developed and compared to AC impedance data previously obtained. The theoretical model predicts that the normalized average medium proton resistivity is intrinsically \((I/C)_v\) dependent and does not depend on the diameter of the support particles. Volumetric \((I/C)_v\) rather than mass \((I/C)_m\) ratio must be used to account for the ionomer swelling. However, the model predicts thicker ionomer coverage of the carbon. Further analysis indicated that the carbon particle roughness and porosity play significant roles for the proton conduction. This model can predict the amount of ionomer absorbed into the pores referenced to the carbon volume, yet it cannot determine the total porosity of the carbon material.

#### SYMBOLS

\[ a \] radius of carbon particle, nm
\( d_c \) carbon density, g/cm\(^3\)
\( d_{\text{mem,dry}} \) density of dry membrane, g/cm\(^3\)
\( d_w \) density of water, g/cm\(^3\)
\( d_{\text{mem,wet}} \) density of wet membrane, g/cm\(^3\)
\( f_t \) factor for electrode thickness calculation, 28±2\(\mu\)m/(mgC/cm\(^2\))
\( M_w \) water molecular weight, 18g/mol
\( rf \) roughness factor
\( R_{H^+,\text{cath}} \) cathode proton resistance, \(\Omega\cdot\text{cm}^2\)
\( T \) temperature, K or °C

Greek
\( \delta \) ionomer thickness, nm
\( \lambda \) water content, mol\(\text{H}_2\text{O}/\text{mol}\text{SO}_3\text{H}\)
\( \rho_{H^+,\text{cath}} \) proton resistivity in the cathode, \(\Omega\cdot\text{cm}\)
\( \rho_{\text{f,film}} \) resistivity of the ionomer in film form, \(\Omega\cdot\text{cm}\)

REFERENCES


Chapter 5

Effects of Catalyst Carbon Support on Proton Conduction and Electrode Performance in PEM Fuel Cells

5.1 INTRODUCTION

Both the anode and the cathode in proton exchange membrane (PEM) fuel cells are composed of porous carbon particles on which Pt is dispersed and covered by a thin layer of ionomer. In Chapters 2 and 3, the effects of ionomer-to-carbon weight ratio (I/C-ratio), relative humidity (RH), and ionomer equivalent weight (EW) on the proton resistance in the cathode \( R_{H^+,\text{cath}} \) have been studied. It was found that for the same operating conditions, carbon support and ionomer, \( R_{H^+,\text{cath}} \) decreases with increasing I/C-ratio. For different EWs, the density of -SO\(_3\)H groups in the electrode is an important parameter influencing the \( R_{H^+,\text{cath}} \). In this Chapter, the effect of the type of carbon support on the proton conduction and the ORR kinetics is investigated. Iden et al.\(^1\) using a H\(_2\)/H\(_2\) cell, studied the effect of carbon support on the proton resistance in a pseudo-electrode mimicking the proton conduction. Boyer et al.\(^2\) also studied the effect of ionomer content on the electrode proton resistance. A major concern for both studies is that the surface properties of the carbon with or without Pt might be different. The technique used in our work is directly applied to Pt dispersed catalyst (can also be applied to electrode without Pt), eliminating the concern. To exclude other factors, we used the impedance method developed in Chapter 2 to measure and compare two types of electrodes with
Pt/Vulcan-XC72 (Pt/V) or Pt/Ketjenblack (Pt/KB), which is also called high surface carbon (HSC). Both carbons are amorphous, but the KB carbon exhibits higher BET surface area. The carbon support is expected to affect the ionomer distribution and thus the electrode performance and durability. Thus understanding the proton transport in electrodes with different carbon supports is of great significance.

5.2 EXPERIMENTAL

Membrane Electrode Assemblies (MEAs)

Two types of cathodes were made with 45.4%wt. Pt/V (TKK, Japan, appeared in Table 2.1) and 45.4%wt. Pt/KB (TKK, Japan). The anodes were made with mixed catalyst (50%Pt/Vulcan, 50%Pt/KB, also from TKK). DE2021® (DuPont, USA) ionomer with 1050 EW was used in all electrodes. MEAs with 50 cm² active areas were fabricated in-house by hot pressing electrode decals onto a 25 μm thick Nafion-211® membranes (DuPont, USA). The diffusion media (DM) are SGL 25BC with microporous layer (MPL) on both sides.

AC impedance and Cell Performance

AC impedance spectra and cell performance were acquired with a Zahner iM6e (Zahner Inc. Germany). H₂/N₂ experiments were used to determine the proton resistance by potentiostating at +0.2 V, with a peak-to-peak perturbation of 2 mV at frequencies ranging from 0.5 to 20,000 Hz. Five spectra were collected at each condition to verify reproducibility. H₂/O₂ cell performance was conducted at 0.1 A/cm² and the voltage data points represent the averaged values over the span of 25min following a precondition for
15 min at 0.1A/cm$^2$. All experiments were conducted at 80°C with four different inlet/outlet RH-values under differential flow conditions (i.e., negligible RH variations). The H$_2$ and O$_2$ partial pressures at each RH-level were maintained constant at 253 kPa$_{abs}$ (at the cell outlet) by varying the total cell pressure: 300, 287, 276, and 269 kPa$_{abs}$ at 122%, 75%, 50%, and 35% RH, respectively. H$_2$ flow rates were held constant at 2100 sccm (standard cubic centimeter per minute), while O$_2$ and N$_2$ flow rates were held constant at 1750 sccm.

5.3 RESULTS AND DISCUSSION

5.3.1 Proton Resistivity: Effect of Catalyst Carbon Support

As mentioned in the introduction, a major difference between Vulcan and Ketjenblack is the carbon surface area. The catalyst specifications, such as Pt weight percentage on the carbon support, the surface area of the Pt, carbon and catalyst, are listed in Table 5.1. The number in parenthesis is the lot number of each catalyst. Table 5.1 shows that Pt/KB has significantly higher surface area in all aspects provided by the manufacturer. The surface area per gram carbon and per gram catalyst is about 3-4 times larger than that of Pt/V. Both catalysts show similar Pt sizes of 2-3 nm, determined by X-ray diffraction (XRD). The Pt surface areas measured by H-adsorption/desorption in fuel cell are also listed in the table, which are 46 and 64 m$^2$/g$_{Pt}$ for Pt/V and Pt/KB, respectively. It shows that the measured Pt areas measured in this work are much smaller than those of provided by the manufacturer using CO adsorption. The difference between two measurement methods could be the reason causing the discrepancy between the measured and provided.
Table 5.1: Catalyst Specifications for Pt/V and Pt/KB catalysts as specified by manufacturer (TKK, Japan).*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%wt. Pt/C</th>
<th>Pt surface area (m²/gPt)</th>
<th>Pt surface area (m²/gPt)**</th>
<th>N₂ BET area (m²/g carbon)</th>
<th>N₂ BET area (m²/g catalyst)</th>
<th>Pt size by XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Vulcan XC72</td>
<td>45.4</td>
<td>73.5</td>
<td>46</td>
<td>250</td>
<td>86.4</td>
<td>2.5</td>
</tr>
<tr>
<td>(106-1331)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/KB</td>
<td>45.4</td>
<td>129.0</td>
<td>64</td>
<td>800</td>
<td>323.1</td>
<td>2.3</td>
</tr>
<tr>
<td>(106-1751)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Catalyst Specification provided by manufacturer (TKK, Japan)
** Measured in the fuel cell in this work

All the electrodes were uniformly made, and analyzed by the same method as stated in Chapter 2. Figures 5.1 a and b, respectively, show the ac impedance spectra of Pt/V and Pt/KB electrodes at I/C-ratio of 0.5. The corresponding imaginary part is also shown in each plot as a function of frequency. The impedance spectrum for each type of electrode agrees well with the model fitting curve, indicating that the ionomer distributes on these two carbon supports in a similar way, despite their different surface areas.

As seen in Figure 5.1, the high frequency resistance (HFR) can be read by extrapolating the high frequency end to the real axis. The ratio between the electrode proton resistance and its capacitance can be obtained from the 45° segment in the spectrum:

\[ \frac{R_{H^+ \text{,cath}}}{C_{\text{cath}}} = \left[ Im(Z) \right]^2 \cdot 4 \cdot \pi \cdot f \equiv \left[ Re(Z) - \text{HFR} \right]^2 \cdot 4 \cdot \pi \cdot f \]  \[5.1\]

where \( Im(Z) \) is the imaginary part of the impedance (Ω·cm²), \( f \) is the corresponding frequency (Hz) and \( Re(Z) \) is the real part of the impedance (Ω·cm²). This ratio is unique for a specific electrode at certain operating conditions.
Figure 5.1: Impedance spectra comparison of electrodes with (a) Vulcan and (b) Ketjen black (KB) carbon supports. Dash-dotted curves represent model fitting Nyquist plots.
$C_{cath}$, the cathode capacitance (mF/cm$^2_{MEA}$), can be obtained from the impedance data$^3$:

$$C_{cath} = \lim_{f \to 0} \left[ \frac{-1}{2 \cdot \pi \cdot f \cdot Im(Z)} \right]$$  \hspace{1cm} [5.2]

Once $C_{cath}$ is available, $R_{H^+,cath}$ is determined by Equation 5.1. All the obtained impedance spectra in this work are analyzed by this method.

$C_{cath}$ can be converted to Pt specific capacitance

$$C_{specific} = \frac{C_{cath}}{L_{Pt,cath} \cdot A_{Pt,el} \cdot 10}$$  \hspace{1cm} [5.3]

where $L_{Pt,cath}$ is the cathode Pt loading in mg$_{Pt}$/cm$^2_{MEA}$, $A_{Pt,el}$ is the Pt specific surface area in m$^2$/g$_{Pt}$ determined from the H-adsorption/desorption charge of cyclic voltammograms, and the factor 10 is a unit conversion factor so that $C_{specific}$ is in unit of mF/cm$^2_{Pt}$. This analysis is conducted for both electrodes. The $C_{specific}$ for all the studied electrodes is shown in Figure 5.2. All data points lie in the range of 0.71 to 0.84 mF/cm$^2_{Pt}$, which is consistent with the results obtained in Chapter 2. This indicates that the Pt-specific capacitance is independent of catalyst carbon support.
Figure 5.2: Pt-specific capacitance versus I/C-ratio for electrodes with Ketjenblack (Δ) or Vulcan (○) carbon support.

Figures 5.3 a and b respectively show the proton resistivity as a function of I/C-ratio for electrodes with Pt/V and Pt/KB at various RHs. The cathode proton resistivity ($\rho_{H^+,cath}$) for each type of electrode strongly depends on the I/C-ratio and RH. The ratios between the two $\rho_{H^+,cath}$ of both electrodes at the same I/C and RH are shown in Figure 5.4. It indicates that at a given I/C and at a certain RH, the resistivity of the Pt/KB electrodes with the higher surface areas is significantly higher than that of the Pt/V electrodes. This result is consistent with a recent report. The ratio ($\rho_{H^+,cath,Pt/KB}/\rho_{H^+,cath,Pt/V}$) lies mostly within the range of 2-3, except at a very dry condition (35%RH) and I/C<0.8. Based on the BET data for each electrode, the resistivity ratio is
expected to be around 3 assuming that all the BET area of each carbon material is accessible to the ionomer. However, due to the higher porosity of KB, a significant portion of the ionomer is probably absorbed inside the particles and consequently, less ionomer contributes to the proton conduction resulting in a higher proton resistance, especially at low I/C or low RH.
Figure 5.3: Electrode proton resistivity vs. I/C ratio for electrodes with (a) Vulcan (b) Ketjenblack carbon support at 122\%, 75\%, 50\% and 35\%RH.
5.3.2 Tortuosity of Ionomer in the Cathodes

As discussed in Chapter 2, the tortuosity, $\tau(\varepsilon_i)$, of a porous medium depends on the ionomer volume fraction $\varepsilon_i$:

$$\tau(\varepsilon_i) = \frac{\rho_{H^+,\text{cath}} \cdot \varepsilon_i}{\rho_{\text{film}}}$$ \hspace{1cm} [5.4]

where $\rho_{\text{film}}$ is the resistivity of the bulk ionomer. In the present work, the same ionomer (DE2021®, 1050EW) is used for all electrodes and the values of $\rho_{\text{film}}$ are taken from
Figure 3.8 at various RHs. The ionomer volume fraction $\varepsilon_i$ in the electrode is derived in Chapter 2 (Equation 2.12)

$$
\varepsilon_i = \left( \frac{I}{C} \right) \cdot \frac{10}{f_t \cdot d_{\text{mem, dry}}} \cdot \left( 1 + \frac{M_w \cdot d_{\text{mem, dry}} \cdot \lambda}{d_w \cdot EW} \right) \quad [5.5]
$$

where $I/C$ is the weight ratio of ionomer to carbon in the electrode, $f_t$ is $28 \pm 2\mu\text{m/(mgC/cm}^2\) for $I/C$ of $<3$, $d_{\text{mem, dry}} \approx 2.1\text{g/cm}^3$, is the density of dry ionomer determined in Chapter 3 (Equation 3.6), $d_w=0.97\text{g/cm}^3$ is the density of water at $80^\circ\text{C}$, $M_w=18\text{g/mol}$ is water molecular weight. $\lambda$ is the number of water molecule per proton, which is calculated from Equation 5.6 (same as Equation 2.2), and $EW= 1042\text{ g/mol}_{\text{H}^+}$ is the equivalent weight of the ionomer in the electrode, as determined in Chapter 3:

$$
\lambda(RH) = \left[ 1 + RH^2 \cdot 0.2352 \cdot \left( \frac{T-30}{30} \right) \right] \cdot \left[ 14.22 \cdot RH^3 - 18.92 \cdot RH^2 + 13.41 \cdot RH \right] \quad [5.6]
$$

where $T$ is temperature in $^\circ\text{C}$. This correlation is valid for temperature between 30 to $95^\circ\text{C}$ at $\text{RH} \leq 80\%$. Combining Equations 5.4-5.6, the obtained tortuosities for the KB and the Vulcan carbon supports are plotted vs. $\varepsilon_i$ in Figure 5.5.

The tortuosity of two electrodes with different carbon support materials is very different. Each of the electrodes shows one single correlation between tortuosity and ionomer volume fraction, i.e., independent of RH. Electrodes with Pt/KB show higher tortuosity than the electrodes with Pt/V at the same ionomer volume fraction. This indicates that in the Pt/KB electrodes, either more ionomer is absorbed into the inner pores of the porous KB carbon or it is distributed on larger surface than the one in the Pt/V electrodes due to its surface roughness.
Figure 5.5: Tortuosity as a function of ionomer volume fraction in cathodes with Pt/V (hollow symbols) and Pt/KB (solid symbols) catalysts and DE2021® ionomer, respectively, at various RHs and at 80°C.

5.3.3 Comparison of Thin Shell Model to Experimental Data

To further understand the large difference in proton resistivity between the Pt/V and Pt/KB cathodes, the thin shell model developed in Chapter 4 is applied here to estimate how much ionomer is absorbed into the inner carbon pores (I/C)_{ab} and its roughness factor (r_f). As shown in Chapter 4, the thin shell model is expressed by

\[
\rho_{H^+,\text{cath}}^{\text{film}} = \frac{\frac{3}{\pi(I/C)_v}}{\ln[1 + \frac{12}{(I/C)_v}]} \quad [5.7]
\]
where \((I/C)_v\) is the ionomer-to-carbon volumetric ratio taking the ionomer swelling into account:

\[
(I / C)_v = (I / C) \frac{d_c}{d_{\text{mem, wet}}} \left(1 + \frac{M_w \lambda}{EW}\right) \tag{5.8}
\]

where \(d_c\) is the carbon density \((2\,\text{g/cm}^3)\), and \(d_{\text{mem, wet}}\), the wet ionomer density, can be estimated by

\[
d_{\text{mem, wet}} = \frac{EW + \lambda M_w}{d_{\text{mem, dry}}} + \frac{M_w \lambda}{d_w} \tag{5.9}
\]

It should be noted that \((I/C)_v\) is related to the ionomer volume fraction, \(\varepsilon_i\), as described by Equation 5.5. The carbon volume fraction \((\varepsilon_C)\) is essentially kept constant and independent of \((I/C)_m\), therefore the \((I/C)_v\) is directly proportional to the ionomer volume fraction. The cathode proton resistivity data appeared in Figure 5.3b are normalized by the \(\rho_{\text{film}}\) \((1050\text{EW})\) as shown in Figure 3.8, and replotted in Figure 5.6. The thin shell model curve is also plotted in Figure 5.6, as illustrated by the solid line. The data values are much higher than the model predictions, indicating that some portion of ionomer is not part of the proton conduction network. Clearly, some other factors need to be incorporated in order to fit the data, such as the roughness or porosity, especially of the Pt/KB electrode. There are three possibilities: the discrepancy is caused by the roughness of the carbon, is caused by its porosity, or is resulted from both effects. If only roughness factor \((rf)\) is taken into account, the thin shell model becomes

\[
\frac{\rho_{H^+, \text{cath}}}{\rho_{\text{film}}} = \frac{3\,(rf)}{\pi (I / C)_v} \ln \left[1 + \frac{12\,(rf)}{(I / C)_v}\right] \tag{5.10a}
\]
If only the porosity is considered, the model becomes

\[
\frac{\rho_{H^{+},cath}}{\rho_{i,film}} = \frac{3}{\pi[(I/C)_v -(I/C)_{ab}]} \ln[1 + \frac{12}{(I/C)_v -(I/C)_{ab}}] \tag{5.10b}
\]

where \((I/C)_{ab}\) represents the amount of ionomer absorbed into the pores. If these two effects are combined, the model is expressed by

\[
\frac{\rho_{H^{+},cath}}{\rho_{i,film}} = \frac{3(rf)}{\pi[(I/C)_v -(I/C)_{ab}]} \ln[1 + \frac{12rf}{(I/C)_v -(I/C)_{ab}}] \tag{5.10c}
\]

The curves determined by Equations 5.10a-c each are plotted in Figure 5.6, illustrated by the dashed curve, dotted curve, and dot-dashed curve, respectively. It is shown that the roughness correction \((rf)=4\) can move the model curve to fit the data at high \((I/C)_v\), while the absorption effect of \((I/C)_{ab}=0.46\) is more effective in matching the model values and the experimental data at low \((I/C)_v\). Nevertheless, neither of them could individually match the data. In Figure 5.6, the dot-dashed curve represents the model prediction by taking both effects into account. Therefore, the discrepancy between the original thin shell model and the experimental data is caused by the carbon roughness and its porosity. The porosity of the carbon cannot be used because some pores are too small to absorb the ionomer. However, the model provides a way to compare different carbon supports by the roughness and the amount of ionomer absorbed. As obtained in Chapter 4, for Pt/V cathodes, the correction for roughness is 1.6 and the \((I/C)_{ab}=0.3\). The proton resistivity of the Pt/KB cathode is 3-4 times higher than of the Pt/V cathode, in agreement with the visual observations that the KB particles are rougher and porous. The present analysis
implies that smooth and nonporous support is preferable from the proton conduction point of view.

![Comparison of normalized experimental proton resistivity for Pt/KB cathodes as a function of ionomer-to-carbon volumetric ratios with different versions of thin shell model with or without considering carbon porosity and roughness.](image)

**Figure 5.6:** Comparison of normalized experimental proton resistivity for Pt/KB cathodes as a function of ionomer-to-carbon volumetric ratios with different versions of thin shell model with or without considering carbon porosity and roughness.

### 5.3.4 Cell Performance: Effect of Catalyst Carbon Support

Cell voltages ($E_{\text{cell}}$) of H₂/O₂ cells measured for both types of electrodes at various RHs are shown in Figure 5.7a. Except for 35%RH, the electrodes with the Pt/KB catalyst show higher $E_{\text{cell}}$ at the same I/C-ratio. As discussed in previous chapters, cell performance is given by

$$E_{\text{cell}} = E_{\text{rev}} - i \cdot HFR - \eta_{\text{HOR}} - \eta_{\text{OBR}} - i \cdot (R_{\text{H}^+,\text{an}}^{\text{eff}} + R_{\text{H}^+,\text{cath}}^{\text{eff}})$$ [5.11]
where $E_{\text{rev}}$ is the reversible cell voltage, determined by the anode and cathode equilibrium potential, temperature, reactant partial pressure and water vapor activity. HFR is the high frequency resistance, which includes the membrane proton resistance and electronic resistance across the cell mainly induced by the contact resistance between the diffusion media and the flow field. The HFR is usually measured by AC impedance by extrapolating the high frequency end of the Nyquist spectrum to the real axis. $\eta_{\text{HOR}}$ is the overpotential of the hydrogen oxidation reaction (HOR), which is usually negligible due to the fast HOR kinetics. On the other hand, the oxygen reduction reaction (ORR) kinetics is about 7 orders slower than the HOR, and the overpotential, $\eta_{\text{ORR}}$, is the most significant voltage loss in the cathode. The two items in the parenthesis respectively stand for the effective proton resistance in the anode and the cathode, which take into account the catalyst utilization effect. The $R_{\text{H}^+,\text{an}}^{\text{eff}}$ is negligible (less than 1.5mV) under this work’s operating condition. The $R_{\text{H}^+,\text{cath}}^{\text{eff}}$ can be obtained from the $R_{\text{H}^+,\text{cath}}$ by

$$R_{\text{H}^+,\text{cath}}^{\text{eff}} = \frac{R_{\text{H}^+,\text{cath}}}{3 + \zeta}$$

where $\zeta$ is a correction factor accounting for the catalyst utilization, which describes the proton effective penetration length into the cathode, determined by the ratio of proton resistance to the ORR charge transfer resistance. Usually, at low current density or low $R_{\text{H}^+,\text{cath}}$, this factor is negligible, thus $R_{\text{H}^+,\text{cath}}^{\text{eff}}$ is $\sim 1/3$ of the proton resistance though the entire thickness of the electrode. $\zeta$ becomes significant when at the product of current density and $R_{\text{H}^+,\text{cath}}$ is high.

Both anodes and cathodes have the same Pt-loading of 0.4mg/cm$^2$, and any difference observed in Figure 5.7a is induced by the ORR and proton resistance in the cathode. As
demonstrated in Figure 5.3, the proton resistance in the cathodes with Pt/KB is much higher than the proton resistance in Pt/V cathodes at the same I/C-ratio. Therefore, the Pt/KB cathodes must possess better catalytic activity for ORR given the same operating conditions (>35%RH) to compensate for the extra loss induced by the proton transport. The ORR kinetics is independent of the I/C-ratio, while the proton resistance increases with decreasing I/C, and it increases faster for the cathode with Pt/KB than the one with Pt/V cathodes, as shown in Figure 5.4 at 35%RH. Actually at 50%RH, the Pt/KB cathode at I/C of 0.5 shows lower performance already. At 35%RH, the Pt/V cathodes demonstrate higher cell voltage.

Omitting the negligible terms, $\eta_{\text{HOR}}$ and $i \cdot R_{\text{H}, \text{an}}^{\text{eff}}$ in Equation 5.11, and rearranging

$$E_{\text{iR-free}} = E_{\text{rev}} - \eta_{\text{ORR}} = E_{\text{cell}} + i \cdot \text{HFR} + i \cdot R_{\text{H}, \text{cath}}^{\text{eff}}$$

[5.13]

where $E_{\text{iR-free}}$ is the voltage corrected for the losses induced by HFR and proton resistance in the cathode, which can also be described as the theoretical voltage excluding the ORR overpotential. Figure 5.7b shows the iR-corrected cell voltage $E_{\text{iR-free}}$ as a function of the I/C-ratio for both types of electrodes at 122%, 75%, 50%, and 35% RH. For Pt/KB cathodes, the data points lie in the range of 0.89 to 0.925V, while for Pt/V cathodes, the data scatter in 0.876 to 0.9V. The plot clearly shows that the $E_{\text{iR-free}}$ of most of the Pt/KB cells are higher than the Pt/V cells. At fully humidified condition, the averaged $E_{\text{iR-free}}$ of Pt/KB cathodes is 0.902V, while the averaged $E_{\text{iR-free}}$ of Pt/V cathodes is 0.895V.
Figure 5.7: Comparison of (a): $E_{cell}$ and (b): $E_{iR-free}$ as a function of I/C-ratio for electrodes with Pt/V and Pt/KB at 0.1 A/cm$^2$ in H$_2$/O$_2$ cells.

The averaged $E_{iR-free}$ for each type of cathodes are plotted in Figure 5.8 as a function of RH. Interestingly, the trends of their $E_{iR-free}$ changing with RH are different: the $E_{iR-free}$ of Pt/KB increases with decreasing RH, while it is nearly independent of the RH for Pt/V cathodes. As shown in Equation 5.13, the $E_{iR-free}$ can also be calculated by subtracting the $\eta_{ORR}$ from the $E_{rev}$. The $E_{rev}$ can be described as$^{11}$

$$E_{rev} = 1.23 - 0.9 \times 10^{-3} (T - 298) + \frac{2.303RT}{4F} \log \left[ \frac{p_{H_2}}{p_{H_2}^*} \right] \left[ \frac{p_{O_2}}{p_{O_2}^*} \right] \left[ \frac{a_{H_2O}^*}{a_{H_2O}} \right]^2 \right]$$ [5.14]
where T is the cell temperature in units of K, R is the universal gas constant (8.314 J/(mol·K)), and F is the Faraday’s constant (96485 C/eq). $p_i$ is the partial pressure with the subscripts denoting the species, and $p_i^*$ represents the corresponding reference partial pressure of 101.3 kPa. $a_{H_2O}$ is the water vapor activity, $a_{H_2O}/a_{H_2O}^* = 1$ for RH≥100%, and $a_{H_2O}/a_{H_2O}^* = RH$ (given as fraction rather than in %) at subsaturated condition.

The $\eta_{ORR}$ is described as

$$\eta_{ORR} = \frac{2.303RT}{\alpha_c F} \log \left( \frac{i + i_x}{10L_{Pt,cath} \cdot A_{Pt,el} \cdot i_{o,s}^* \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^\gamma} \right) \tag{5.15}$$

where $\alpha_c$ is the cathodic transfer coefficient with a determined value of, $\alpha_c = 1$, $i_x$ is the H₂ crossover current in unit of A/cm², $i_{o,s}^*$ (A/cm²_Pt) is the catalyst-specific exchange current density normalized to reference oxygen partial pressure ($p_{O_2}^*$) of 101.3 kPa at the reference temperature ($T^*$) of 80°C, and $\gamma (0.54)^8$ is the kinetic reaction order with respect to oxygen partial pressure. In Chapter 2, the $i_{o,s}^*$ for Pt/V catalyst has been determined as $(1.5\pm0.2)\times10^{-8}$ A/cm²Pt. Here, the same analysis is conducted on the Pt/KB catalyst, and the obtained $i_{o,s}^*$ is $(1.7\pm0.2)\times10^{-8}$ A/cm²Pt. The averaged electrochemical area $A_{Pt,el}$ of the Pt/KB cathodes is 64m²/gPt, while the averaged $A_{Pt,el}$ of the Pt/V cathodes is 46m²/gPt. The difference between the $i_{o,s}^*$ and the $A_{Pt,el}$ of these two catalysts results in ~12mV extra ORR overpotential for Pt/V cathodes, given the same nominal cathode Pt loading. This is
consistent with the difference between the experimental values of $E_{iR-free}$ for these two cathodes at fully humidified condition, as shown in Figure 5.7b.

Inserting Equations 5.14 and 5.15 into the middle of Equation 5.13, the theoretical values for the $E_{iR-free}$ of each type of cathodes are plotted in Figure 5.8, where $E_{iR-free}$ of both cathodes increases with decreasing RH. At the same RH, the averaged $E_{iR-free}$ of Pt/KB cathode is consistently higher than that of the Pt/V cathode by ~8mV. This observation is considered resulting from the different Pt dispersion on the two carbon supports. The experimentally obtained $E_{iR-free}$ are also plotted in Figure 5.8, however their trends with RH are different. On one hand, the measured $E_{iR-free}$ of Pt/KB catalyst matches the calculation very well, except for 35%RH, where there is a <10mV difference. On the other hand, the experimental values of the Pt/V cathodes are almost independent of the RH, though there is ~9mV difference between saturated and subsaturated conditions. As discussed in Chapter 2, the difference between the calculated and the measured $E_{iR-free}$ indicates the dependence of $\eta_{ORR}$ on the RH. Though Figure 5.8 shows some ORR dependence on RH for Pt/V catalyst, the difference is rather small. In all, no clear conclusion can be drawn on the correlation between $\eta_{ORR}$ and RH for each catalyst; however it is clear that the ORR dependence on RH is very weak under studied conditions.
5.4 SUMMARY

The effect of carbon supports on cathode proton resistivity is studied by the comparison between cathodes with Vulcan and KB carbon-supported Pt catalysts, both with the same ionomer. At the same I/C, the Pt/KB cathodes show much higher proton resistivity and tortuosity than the Pt/V cathodes because of its higher carbon surface area and porosity. This is confirmed by the thin shell model considering the effects of roughness and porosity on the proton resistivity. More ionomer is absorbed into the pores of the Pt/KB cathode than the Pt/V cathode, resulting in thinner ionomer layer and higher
resistance. However, no conclusion can be drawn on the porosity of each carbon material. Though the Pt/KB cathode proton resistance is higher, its cell voltage is higher than Pt/V cathode at RH $\geq 50\%$RH due to its higher catalytic activity and higher Pt electrochemical area. However, at drier conditions, when the gain of Pt/KB catalyst in ORR kinetics cannot compensate for the cathode proton resistance, Pt/KB shows lower cell voltage. The comparison of the calculated iR-corrected cell voltage with the measured values for each cathode indicates that the ORR kinetics should not have a strong dependence on RH if at all. Both the thin shell model and the comparison between Pt/KB and Pt/V show the importance of carbon roughness and porosity. Smooth non porous carbon support is preferable from the proton conduction point of view.

**SYMBOLS**

\( A_{\text{Pt,el}} \)\( \) electrochemical available Pt surface area, \( \text{m}^2_{\text{Pt/gPt}} \)
\( a_{H_2O} \)\( \) water vapor activity
\( a^*_{H_2O} \)\( \) reference water activity, assigned an arbitrary value of 1 at RH $\geq 100\%$
\( C_{\text{cath}} \)\( \) cathode capacitance, \( \text{F/cm}^2_{\text{MEA}} \)
\( C_{\text{specific}} \)\( \) Pt-specific capacitance, \( \text{mF/cm}^2_{\text{Pt}} \)
\( d_c \)\( \) carbon density, \( \text{g/cm}^3 \)
\( d_{\text{mem,dry}} \)\( \) density of dry membrane, \( \text{g/cm}^3 \)
\( d_w \)\( \) density of water, \( \text{g/cm}^3 \)
\( d_{\text{mem,wet}} \)\( \) density of wet membrane, \( \text{g/cm}^3 \)
\( E_{\text{cell}} \)\( \) cell voltage, \( \text{V} \)
\( E_{\text{iR-free}} \)\( \) iR-free cell voltage, cell voltage plus corrections from the proton resistance in cathode and high frequency resistance, \( \text{V} \)
\( E_{\text{rev}} \)\( \) reversible cell potential (function of \( T, p_{H_2}, p_{O_2}, \text{RH} \)), \( \text{V} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>frequency, Hz</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant, C/equiv</td>
</tr>
<tr>
<td>$f_t$</td>
<td>factor for electrode thickness calculation, $28\pm2\mu\text{m}/(\text{mgC/cm}^2)$</td>
</tr>
<tr>
<td>$i$</td>
<td>current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i^*_{o,s}$</td>
<td>exchange current density referenced to $80^\circ\text{C}$ and 101.3 kPa of oxygen partial pressure, based on Pt surface area, A/cm$^2_{\text{Pt}}$</td>
</tr>
<tr>
<td>$i_x$</td>
<td>ORR current density associated with H$\text{2}$ crossover from anode to cathode, A/cm$^2$</td>
</tr>
<tr>
<td>$L_{\text{Pt,cath}}$</td>
<td>cathode Pt loading, mgPt/cm$^2$</td>
</tr>
<tr>
<td>$M_w$</td>
<td>water molecular weight, 18g/mol</td>
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<tr>
<td>$p_{H_2}$</td>
<td>H$\text{2}$ partial pressure, kPa</td>
</tr>
<tr>
<td>$p^*_{H_2}$</td>
<td>reference H$\text{2}$ partial pressure, 101.3 kPa</td>
</tr>
<tr>
<td>$p_{O_2}$</td>
<td>O$\text{2}$ partial pressure, kPa</td>
</tr>
<tr>
<td>$p^*_{O_2}$</td>
<td>reference O$\text{2}$ partial pressure, 101.3 kPa</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, 8.314 J/(mol·K)</td>
</tr>
<tr>
<td>$r_f$</td>
<td>roughness factor</td>
</tr>
<tr>
<td>$R^+_{H^+,\text{cath}}$</td>
<td>cathode proton resistance, $\Omega$·cm$^2$</td>
</tr>
<tr>
<td>$R^{\text{eff}}_{H^+,\text{an}}$</td>
<td>effective proton resistance in the anode, $\Omega$·cm$^2$</td>
</tr>
<tr>
<td>$R^{\text{eff}}_{H^+,\text{cath}}$</td>
<td>effective proton resistance in the cathode, $\Omega$·cm$^2$</td>
</tr>
<tr>
<td>$R_{\text{mem}}$</td>
<td>average membrane resistance, $\Omega$·cm$^2$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K or °C</td>
</tr>
<tr>
<td>$T^*$</td>
<td>reference temperature, 80°C or 353 K</td>
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</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
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<tr>
<td>$\alpha_c$</td>
<td>cathode transfer coefficient</td>
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<tr>
<td>$\varepsilon_i$</td>
<td>ionomer volume fraction</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>ORR order with respect to O$\text{2}$ partial pressure at constant overpotential</td>
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<td>$\eta_{\text{HOR}}$</td>
<td>overpotential of the HOR, V</td>
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<tr>
<td>$\eta_{\text{ORR}}$</td>
<td>overpotential of the ORR, V</td>
</tr>
<tr>
<td>$\eta_t$</td>
<td>transport loss, V</td>
</tr>
</tbody>
</table>
$\lambda$  
water content, $\text{mol}_{\text{H}_2\text{O}}/\text{mol}_{\text{SO}_3\text{H}}$

$\rho_{H^+,\text{cath}}$  
proton resistivity in the cathode, $\Omega\cdot\text{cm}$

$\rho_{\text{film}}$  
resistivity of the ionomer in film form, $\Omega\cdot\text{cm}$

$\tau$  
tortuosity

$\zeta$  
correction factor for reduced cathode proton transport length to membrane

**REFERENCES**


Chapter 6

Determination of Local Electrode Relative Humidity (RH) in a H₂/O₂ Cell

6.1 INTRODUCTION AND MOTIVATION

In a H₂-O₂ PEM fuel cell, water and heat are generated in the cathode, and transported or dissipated in the cathode and anode flow fields (FFs). Water is transported in the membrane via electro-osmotic water drag from the anode to the cathode, and back by diffusion from the cathode to the anode. Therefore, the local relative humidity (RH) in the membrane and electrodes might be significantly different from the RH in the FFs, especially when operating at high current density and low FF channel RH. Typically, water content greatly affects the proton transport in the membrane and electrode,¹,² and consequently affects the catalyst utilization³ and oxygen reduction reaction (ORR) kinetics²,⁴. By knowing the local RH, one can identify possible local dryout and flooding and predict voltaic performance. Thereby, it is very important to know the water distribution across the cell.

Direct measurement of the local RH is very difficult, if not impossible. A recent publication⁵ discussed a method of measuring membrane and cathode proton resistance to predict average local RH in a H₂/N₂ cell, with non-equal RH for the anode and the cathode FF. Since no water production occurs in the cathode, there is actually no need for any water transport properties in order to determine the local RH. Though it is shown that in an operating cell the magnitude of RH changes in the membrane and the electrode
depends on the current density, no clear method was defined. Gu et al.\(^6\) describe a pseudo-2-D model to obtain the reactant concentrations, RH and pressure changes down the flow channel in H\(_2\)/Air cells in a stack level. The present work is designed to eliminate the variations in the down-the-channel direction by operating in a H\(_2\)/O\(_2\) cell under differential condition (uniform RH, reactant partial pressure and current density over the active area of the cell). This allows a 1-D model to predict the local RH in the membrane and the cathode.

The present work is both theoretical and experimental: we first introduce a 1-D model for water transport to predict the local RH in an operating H\(_2\)/O\(_2\) cell as a function of current density and RH of the FF channels. Experimentally, the membrane resistance is measured by AC impedance, and compared with the theoretical prediction. The cell performance is then predicted based on the local RH, and compared with experimental data. The sensitivity of variation in the measured water transport properties is tested, and the prediction of local RH in the cathode is further discussed.

### 6.2 EXPERIMENTAL

Membrane Electrode Assemblies (MEAs)

Limited by the current capability of the instrument and the experimental requirement of differential operating conditions, MEAs with 5 cm\(^2\) active areas were designed to meet the requirement. The schematic of the architecture of the MEA and cell is shown in Appendix C. MEAs were fabricated in-house by hot pressing electrode decals onto 32 µm thick 3M\(^{®}\) membranes with 800 EW. The ionomer (DE2021\(^{®}\)) used in the electrodes had 1050 EW. Both anode and cathode Pt loadings were \(\sim 0.4\) mg\(_{\text{Pt}}\)/cm\(^2\) and had an I/C-
ratio of 0.8, using a ~50%wt Pt/Vulcan XC72 catalyst (Tanaka, Japan). For I/C-ratios of <3, the thickness of electrodes with Vulcan supports depends only on the carbon loading of the electrode and can be calculated from the carbon loading multiplied by 28 µm/(mgC/cm² electrode).

AC Impedance Measurements

Cell performance and high frequency resistances (HFR) are determined at each current density by AC impedance acquired with a Zahner iM6e (Zahner Inc., Germany) in an H₂/O₂ cell. The impedance spectra are obtained by applying certain current density (0.05, 0.1, 0.2, 0.6, 1.0, 1.5 and 2A/cm²) with a perturbation of 0.01A/cm². In H₂/N₂ experiments the N₂-fed working electrode (“cathode”) is potentiostated at +0.2 V vs. the H₂-fed counter/reference electrode (“anode”), with a voltage perturbation of 1 mV (amplitude) at frequencies ranging from 0.5 to 20,000 Hz. Five spectra are collected at each condition to verify reproducibility. In the case of H₂/O₂ experiments, the H₂ and O₂ partial pressures at each RH-level at 80°C were maintained at 253 kPaabs (at the cell outlet) by varying the total cell pressure: 300 kPaabs at 122%RH, 287 kPaabs at 75% RH, 276 kPaabs at 50% RH, 269 kPaabs at 35% RH, and 264 kPaabs at 25% RH. H₂, N₂, and O₂ flow rates were held constant at 3500 sccm.

6.3 RESULTS AND DISCUSSION

6.3.1 1-D Water Fundamental Transport Model

6.3.1.1 Model Description

The humidified H₂ and O₂ are respectively fed to the anode and cathode FF channels
at certain temperature, establishing the boundary conditions there. Figure 6.1 shows a schematics of the various gaseous partial pressures, RH and temperature profiles across the cell. The dashed vertical lines are the interfaces between each component, and the dotted lines represent the molecular H₂ and O₂ crossover profiles in the membrane. The production of water in the cathode produces heat, resulting in RH and temperature gradients between the electrode and the FF. Water generated in the cathode is transported via gas phase toward the cathode FF and back diffuses through the membrane toward the anode side, overcoming the electro-osmotic drag.

**Figure 6.1:** A schematic of gaseous species partial pressures, RH and temperature profile across the cell sandwich.

In what follows, the details to obtain water vapor pressure in the anode and the cathode are presented. Under steady state, water is transported from anode FF to the
anode catalyst layer (CL) via convective transport through FF channel, followed by
diffusive transport through the DM and the anode. The total water flux \(N_{\text{H}_2\text{O,FF-CL,an}}\) is
described by \(6\)

\[
N_{\text{H}_2\text{O,FF-CL,an}} = \frac{(P_{\text{H}_2\text{O,FF,an}} - P_{\text{H}_2\text{O,CL,an}})}{R_{\text{H}_2\text{O,FF-CL,an}}} \frac{RT}{\beta_{\text{H}_2\text{O}}}
\]

[6.1a]

Analogously, water flux from cathode CL to FF is

\[
N_{\text{H}_2\text{O,FF-CL,cath}} = \frac{(P_{\text{H}_2\text{O,CL,cath}} - P_{\text{H}_2\text{O,FF,cath}})}{R_{\text{H}_2\text{O,FF-CL,cath}}} \frac{RT}{\beta_{\text{H}_2\text{O}}}
\]

[6.1b]

In the membrane, water flux is the combination of drag by protons and back diffusion
from the cathode CL towards the anode CL

\[
N_{\text{H}_2\text{O,mem}} = \frac{\rho}{\text{EW}} \frac{\lambda_{\text{an}} - \lambda_{\text{cath}}}{R_{\text{H}_2\text{O,mem}}} + \frac{\xi}{F} \frac{i}{F}
\]

[6.1c]

At steady state, the sum of the water flux entering the cathode and produced by the ORR
should be equivalent to what is leaving towards cathode FF, which is

\[
N_{\text{H}_2\text{O,FF-CL,an}} + \frac{i}{2F} = N_{\text{H}_2\text{O,FF-CL,an}} = 0
\]

[6.1d]

where \(R\) is the universal gas constant (8.314 J/(mol·K)), \(\rho\) is the partial pressure (kPa)
with species and location as subscripts, \(i\) is the current density, and \(F\) is Faraday’s
constant (96485 C/eq). \(R_{\text{H}_2\text{O}}\) is the water transport resistance at various locations. \(\rho\) is
the dry membrane density (g polymer/cm\(^3\)), EW is the membrane equivalent weight
\((g_{\text{polymer/molSO}_3H})\), and \(\xi\) is the electro-osmotic drag coefficient. \(\lambda\) is the number of water per proton (mol\(H_2O/molH^+\)) at the membrane/electrode interface, which can be calculated by\(^7\)

\[
\lambda(RH) = \left[1 + RH^2 \cdot 0.2352 \cdot \left(\frac{T - 30}{30}\right)\right] \cdot \left(14.22 \cdot RH^3 - 18.92 \cdot RH^2 + 13.41 \cdot RH\right) \tag{6.2}
\]

where \(RH\) is defined as fraction rather than percentage as shown in Equation 6.3

\[
RH = \frac{p_{H_2O}}{p_{\text{sat}}^{H_2O}(T)} \tag{6.3}
\]

and the saturated water vapor pressure \(p_{\text{sat}}^{H_2O}\) is given as a function of temperature \(T\) (in unit of °C) by\(^8\)

\[
\log(p_{H_2O}^{\text{sat}}/\text{atm}) = -2.1794 + 0.029535T - 0.000091838T^2 + 0.00000014454T^3 \tag{6.4}
\]

Equation 6.2 is valid for a wide range of sulfonic acid ionomers within \(RH=0.1\) (10%) to \(RH=0.8\) (80%) and at the temperature \(T\) (in unit of °C) between 30 to 95°C. Beyond 80%RH, different equations would be needed for each type of ionomer.\(^7\) In the present work, the water diffusivity in the membrane is estimated by Equation 6.4 for \(RH\leq100\%\).

The transport resistance appeared in Equations 6.1 a-c is each described by\(^6\)

\[
R_{H_2O,FF-CL,an} = \frac{1}{h_{H_2O,FF,an}} + \frac{f_{DM,an} \delta_{DM,an}}{D_{H_2O,DM,an}^{\text{eff}}} + \frac{\delta_{CL,an}}{D_{H_2O,CL,an}^{\text{eff}}} \tag{6.5a}
\]
\[
R_{H_2O,FF-CL,cath} = \frac{1}{h_{H_2O,FF,cath}} + \frac{f_{DM,cath}\delta_{DM,cath}}{D_{H_2O,DM,cath}} + \frac{\delta_{eff,cath}}{D_{H_2O,CL,cath}} 
\]  

[6.5b]

\[
R_{H_2O,mem} = \int_0^{\delta_{mem}} \frac{dx}{D_{H_2O,mem}} 
\]  

[6.5c]

In Equations 6.5 a and b, \( f_{DM} \) is the geometric correction factor accounting for the effect of FF lands on the water transport length from the FF channel to the electrode. \( \delta \) is the diffusive layer thickness with subscripts denoting the DM or CL. \( \delta_{eff,cath} \) \((\sim 2/3\delta_{CL,cath})\) represents the effective water diffusion layer thickness in the cathode CL considering the production of water. \( h_{H_2O} \) is the convective mass transfer coefficient at the FF/DM interface. Appendix D shows that the flow in each FF channel is laminar under all operating conditions, and subsequently the \( h_{H_2O} \) can be estimated from the Sherwood number \( (Sh) \) for laminar flow in a duct \(^9\)

\[
Sh = \frac{h_{H_2O}d}{D_{H_2O}} = 2.693 
\]  

[6.6]

where \( d \) (cm), the characteristic length, is the FF channel depth. \( D_{H_2O} \), the water diffusivity, normally only includes the water diffusion in the medium via molecular diffusion. However, in porous media where the pore size is comparable to the mean free path of the \( H_2O \) molecule, Knudsen diffusion becomes significant and has to be considered while calculating the \( D_{H_2O} \) defined as \(^{10}\)

\[
D_{H_2O} = \left( \frac{1}{D_{K,H_2O}} + \frac{1}{D_{H_2O,mix}} \right)^{-1} 
\]  

[6.7a]
Here, $D_{K,H2O}$ is the Knudsen diffusion coefficient:\(^{11}\)

$$D_K = \frac{2}{3} \left( \frac{8RT}{\pi M} \right)^{1/2} r_p$$ \[6.7b\]

where $R$ is the universal gas constant (8.314×10\(^7\) g·cm\(^2\)/s\(^2\)·g-mol·K), $T$ is the temperature in unit of K, $r_p$ is the mean pore radius of the porous medium in unit of cm, and $M$ is the molar molecular weight of the diffusing species, which is 18 g/g-mol in this case for H\(_2\)O. In the DM, the pore size is on the scale of μm so the Knudsen diffusion is negligible. $r_p$ in the electrodes and the micro porous layer (MPL) is ~25nm, therefore, $D_K = 0.11$ cm\(^2\)/s at 80°C. The molecular diffusion coefficient, $D_{H2O, mix}$, in a binary mixture (in this case it is H\(_2\)O and H\(_2\) or H\(_2\)O and O\(_2\) mixture) can be obtained by\(^{12}\)

$$D_{i,j} = \frac{1.00 \times 10^{-3} \times T^{1.75}}{p \times (v_i^{1/3} + v_j^{1/3})^2} \times \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}$$ \[6.7c\]

where $p$ is the total pressure in unit of atm, $T$ is the temperature in K, $v$ is the diffusion volume ($v_{H2O}$ is 12.7, $v_{H2}$ is 7.07 and $v_{O2}$ is 16.6 cm\(^3\)/g-mol\(^{12}\), and $M$ is the component molecular weight. At 80°C, the $D_{H2O,H2}$ is ~0.40, and $D_{H2O,O2}$ is ~0.12 cm\(^2\)/s. In Equation 6.6, only 6.7c is needed to estimate the $D_{H2O}$.

In Equations 6.5 a and b, $D_{eff}^{H2O}$ (cm\(^2\)·s\(^{-1}\)) is the effective diffusivity of water in the DM and the electrode, which is generally affected by the porosity ($\varepsilon$) and tortuosity ($\tau$) of a porous medium\(^{6}\)

$$D_{eff}^{H2O} = D_{H2O} \times \frac{\varepsilon}{\tau}$$ \[6.8\]
\( \tau / \varepsilon \) (equivalent to \( D / D_{\text{eff}} \)) is a geometric property of the porous material, and can be experimentally estimated by a limiting current method, which is used to measure the \( O_2 \) transport resistance in PEM fuel cells.\textsuperscript{13} In principle, \( D_{H_2O} \) in DM and MPL should be separately estimated due to the existence of the Knudsen diffusion in the MPL if the transport resistance in the MPL can be extracted, as described in Ref. 6 and 13 while using Toray DM, when the transport resistance from MPL is quite small. However, if the transport resistance in the MPL is substantial so that \( D / D_{\text{eff}} \) for the DM itself is difficult to be determined, under this circumstance, a lumped \( D / D_{\text{eff}} \) will be applied considering the DM and the MPL as one component.\textsuperscript{13} This is the case for SGL DM, which is used on both the anode and the cathode in this work.

Having determined the water diffusivity in the FF, DM and electrode, the \( R_{H_2O,FF-CL,an} \) (Equation 6.5a) and \( R_{H_2O,FF-CL,cath} \) (Equation 6.5b) can be obtained. To determine \( R_{H_2O,mem} \) (Equation 6.5c), the water diffusivity in the membrane, \( D_{H_2O,mem} \) (cm\(^2\)/s), is needed. It can be measured by performing water balance across the studied membrane with different RHs on each side under differential condition and at zero current. According to GM’s unpublished results, the water diffusivity for 3M membrane (800EW) is described by

\[
D_{H_2O,mem} = 10^{-6} \times \begin{cases} 
3.327 \lambda \left[ -1 + 1.619 \exp(0.000935 \lambda) \right] & \text{for } \lambda \leq 4.4 \\
0.1 \lambda \left[ 1 + 70 \exp(-0.3 \lambda) \right] & \text{for } \lambda > 4.4
\end{cases}
\]  

As indicated in Equation 6.2, \( \lambda \) is a function of RH and temperature. RH also depends on temperature. Therefore, local temperature has to be determined where the water
content needs to be known. Due to the ORR in cathode, heat is produced and dissipated to the cathode FF and across the membrane to the anode. At FF temperature of 80°C and applied current density of 1.5A/cm², the cathode temperature is increased by ~6°C, and this temperature is proportional to the current density. The total amount of heat rate per unit area generated within the MEA (W/cm²), mainly is the sum of the irreversible heat generated by the reaction and the reversible heat resulted from the entropy change for the overall reaction, which is almost all generated on the cathode due to the ORR. The heat rate can be roughly calculated by

\[ q = i(E_{rev} - E_{cell}) + i(-T \frac{\partial E_{rev}}{\partial T}) \]  \hspace{1cm} [6.10a]

Noted that equation 6.10a is really from \( \Delta G = \Delta H - T\Delta S \). \( E_{rev} \) is the thermodynamic reversible cell voltage, which is a function of temperature, and partial pressure of \( O_2 (p_{O_2}, \text{in unit of kPa}) \) and \( H_2 (p_{H_2}, \text{in unit of kPa}) \) normalized to the corresponding reference \( O_2 \) and \( H_2 \) partial pressure \( (p_{O_2}^*, p_{H_2}^*) \) of 101.3 kPa, which can be described as

\[ E_{rev} = 1.23 - 0.8456 \times 10^{-3}(T - 298) + \frac{2.303RT}{4F} \log \left( \frac{p_{H_2}}{p_{H_2}^*} \right) \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^2 \]  \hspace{1cm} [6.10b]

where \( T \) is temperature in unit of K, and \( R \) is the universal gas constant (8.314 J/(mol·K)).

In Equation 6.10a \( E_{cell} \) (V) is the cell voltage at certain current density \( i \) (A/cm²). At 1.5A/cm², \( E_{cell} \) is around 0.6V, so \( q = 1.3 \text{W/cm}^2 \). Generally, about 50% of the heat is dissipated via the membrane to the anode side. The temperature difference drop in the membrane (\( \Delta T_{mem} \)) is given by
\[ \Delta T_{\text{mem}} = 0.5q \cdot R_{T,\text{mem}} \]  \hspace{1cm} [6.10c]

where \( R_{T,\text{mem}} \) is the thermal resistance of the dry membrane, which is \( 1.1 \text{ cm}^2 \cdot \text{K/W} \). So the upper limit for the temperature difference across the membrane is \( \Delta T_{\text{mem}} \sim 0.7^\circ \text{K} \) (or \( ^\circ \text{C} \)). Therefore, this work considers no temperature variation within the MEA. The local RH is calculated based on the local temperature.

Figure 6.2 shows the schematic of a 1-D cell model extending from the anode FF to cathode FF. In this model, FF, DM and electrode are considered as one control volume each, while the membrane, because water diffusion is a function of water content which could change significantly across the membrane, is divided into five control volumes in order to accurately describe the water profile, as shown in the scheme. The RH at the center of each control volume is regarded as its average RH. The RH of the anode and the cathode each is considered as uniform, and at the interface of CL/membrane the RH is equal to the electrode RH. \( N_{\text{H}_2\text{O,FF,an(cath)}} \) is the water flux in the FF of the anode or the cathode.

\[ N_{\text{H}_2\text{O,FF,an}} \quad \text{in} \quad \text{FF} \quad \text{DM} \quad \text{Anode Membrane Cathode DM FF} \quad \text{out} \]

\[ CL/\text{mem,an} \quad CL/\text{mem,cath} \]

\[ N_{\text{H}_2\text{O,FF,cath}} \quad \text{in} \quad \text{FF} \quad \text{DM} \quad \text{Anode Membrane Cathode DM FF} \quad \text{out} \]

**Figure 6.2**: Schematic of a 1-D cell model across the cell sandwich. FF, DM and electrode were considered as one control volume each, and membrane is divided into five control volumes.

For the membrane, based on Equations 6.1c, 6.5c and 6.9, the water flux across the \( (\text{CL/membrane})_{\text{an}} \) and location 1 can be calculated by
Analogous treatments are performed on the other membrane control volumes; each can be described by Equations 6.11 b-f.

\[ N_{H_2O,mem,1-2} = \frac{D_{H_2O,mem,1} \cdot D_{H_2O,mem,2}}{D_{H_2O,mem,1} + D_{H_2O,mem,2}} \cdot \frac{\rho(\lambda_{mem,1} - \lambda_{mem,2})}{EW(\delta_{mem}/5)/2} + \xi_{1} \cdot \frac{i}{F} \]  

\[ N_{H_2O,mem,2-3} = \frac{D_{H_2O,mem,2} \cdot D_{H_2O,mem,3}}{D_{H_2O,mem,2} + D_{H_2O,mem,3}} \cdot \frac{\rho(\lambda_{mem,2} - \lambda_{mem,3})}{EW(\delta_{mem}/5)/2} + \xi_{2} \cdot \frac{i}{F} \]  

\[ N_{H_2O,mem,3-4} = \frac{D_{H_2O,mem,3} \cdot D_{H_2O,mem,4}}{D_{H_2O,mem,3} + D_{H_2O,mem,4}} \cdot \frac{\rho(\lambda_{mem,3} - \lambda_{mem,4})}{EW(\delta_{mem}/5)/2} + \xi_{3} \cdot \frac{i}{F} \]  

\[ N_{H_2O,mem,4-5} = \frac{D_{H_2O,mem,4} \cdot D_{H_2O,mem,5}}{D_{H_2O,mem,4} + D_{H_2O,mem,5}} \cdot \frac{\rho(\lambda_{mem,4} - \lambda_{mem,5})}{EW(\delta_{mem}/5)/2} + \xi_{4} \cdot \frac{i}{F} \]  

\[ N_{H_2O,5-mem/CL} = \frac{D_{H_2O,mem,5} \cdot D_{H_2O,mem/CL,cath}}{D_{H_2O,mem,5} + D_{H_2O,mem/CL,cath}} \cdot \frac{\rho(\lambda_{mem,5} - \lambda_{mem/CL,cath})}{EW(\delta_{mem}/5)/2} + \xi_{5} \cdot \frac{i}{F} \]  

In the above equations, \( \xi \) is considered as 1 everywhere in the membrane.\(^{18,19} \)

Having all the Equations 6.1 a, b, d, and 6.11 a-f, the local RH at each specified location shown in Figure 6.2 can be obtained by solving Equation 6.1d iteratively using Newton’s method\(^{20} \) embedded in Excel Solver package. All the required geometric and structure information of the FF, electrode, membrane and DM is tabulated in Table 6.1.

**Table 6.1:** Geometric and structure information of the FF, electrode, membrane and DM.
<table>
<thead>
<tr>
<th>Geometric parameter</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF land/channel ratio</td>
<td>0.77 (0.65mm/0.84mm)</td>
<td>0.77 (0.65mm/0.84mm)</td>
</tr>
<tr>
<td>FF channel depth (mm)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>DM (including MPL) thickness (μm)</td>
<td>176</td>
<td>176</td>
</tr>
<tr>
<td>Electrode thickness (μm)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Electrode I/C-ratio</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>(\epsilon/\tau)_{DM} in Equation 6.8</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>(\epsilon/\tau)_{electrode} in Equation 6.8</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>((r_p)_{electrode}) in Equation 6.7b (nm)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Membrane</td>
<td>32 μm thick 3M® membranes with EW of 800</td>
<td></td>
</tr>
</tbody>
</table>

The above water transport model was solved for various operating conditions. An example of predicted water profile across the cell from the anode FF to the cathode FF is shown in Figure 6.3, operating under the extreme dry condition of 25%RH and high current density of 2A/cm². The inset is the enlarged water profile within the MEA. It indicates that under this condition, the local cathode RH can reach over 85%, while at the anode, the RH drops to ~20%. Under the same cell temperature and FF channel RH, as shown in Figure 6.4, increasing the current density to 3A/cm² results in cathode RH ~102% and anode RH ~18%; only when applying current density as high as 5A/cm² (not shown in Figure 6.4), complete dryout is expected in the anode. Here, dryout is defined as the condition where \(\lambda < 1\) or RH < 10%. If \(\lambda < 1\), the drag coefficient is not 1 anymore, so the equations involved in the model might not be valid. The opposite of dryout is oversaturation, where liquid water starts to form. In the present work, it is regarded to occur at RH>100%. At the 25% FF channel RH, the cathode is actually oversaturated already at ~ 4A/cm² (not shown here). Therefore, cathode saturation is expected to occur.
much earlier than anode dryout, given the materials used in this work. Further analysis shows that when the RH at the channel is 25% at 80°C, the anode RH can drop to <10% when a 65-μm-thick membrane is used at 2A/cm². This dryout results from the poor water back diffusion from the cathode to the anode in comparison to the opposite electro-osmotic drag effect. The dramatic change in the RH across the cell further illustrates the necessity for determining the water profile in an operating cell.

Figure 6.3: Water profile predicted by the 1-D model from anode FF to cathode FF at RH_{FF,an}=RH_{FF,cath}=25%RH and 2A/cm² (H₂/O₂ Stoic=50/100) in a H₂/O₂ cell at 80°C.
Figure 6.4: Local RH in the anode (solid curve) and the cathode (dashed curve), and fraction of water (dotted curve) in terms of produced water transported to cathode FF as a function of current density at various FF channel RHs at 80°C (RH_{FF,an}=RH_{FF,cath}). Dryout occurs when RH<10%; liquid water forms at RH>100%. $p_{H_2, FF}=p_{O_2, FF}=253\text{kPa}$ unless it is specified.

6.3.1.2 Water Removal from Cathode

Figure 6.4 shows the predicted local RHs in the anode and cathode at each RH of the FF channel under a wide range of current densities. The solid and dashed curves represent the anode and cathode RH at $p_{H_2, FF}=p_{O_2, FF}=253\text{kPa}$, respectively. It indicates that the anode RH decreases with increasing current density, while the cathode RH increases with increasing the current density. The RH range between two dash-dotted red lines is considered free of dryout and liquid water in the anode and cathode, respectively.
From the plot one can see that no dryout occurs below 2A/cm², while for the cathode at 75%RH and when the current density reaches 1.5A/cm² liquid water formation is expected there. It should be noted that the temperature and gas pressure have significant effects on where and when the dryout or oversaturation occurs. Decreasing cell temperature causes the cathode to reach saturation at lower current density, while decreasing the gas pressure causes an anode dryout to takes place at a lower current density. In Figure 6.4, the double-dash-dotted curve demonstrates the cathode RH as a function of current density at a cell temperature of 70°C, which results in liquid water formation in the cathode at only ~0.8A/cm², half than when the cathode is saturated at 80°C. If the gas partial pressure is reduced from 253kPa to 153kPa, the anode RH decreases faster with the current densities than at a higher pressure, as shown by the double-dashed curve at 25% FF channel RH.

Having determined the water distribution across the cell, it is of interest to know the amount of water that goes to the cathode FF. Here we introduce a new term, $f_{H_2O}$, to represent the amount of water transported to the cathode FF in terms of the electrochemically produced water at the cathode:

$$f_{H_2O} = \frac{N_{H_2O,FF-CL,cath}}{i/2F} \quad [6.12]$$

Figure 6.4 shows the calculated $f_{H_2O}$, represented by the dotted curves, as a function of current density at 80°C, for channel RH of 75%, 50%, 35%, and 25%. For the previously discussed case (25%RH, 2A/cm²), ~95% of the product water is transported to the cathode FF. When $f_{H_2O} > 1$, the net water flux from the membrane to the cathode is positive, implying that water dragged by electro-osmosis exceeds the back diffusion.
In the RH model it is assumed that water reaches the cathode FF as vapor. The flux of water vapor transported to the cathode FF, \( v_{H_2O} \), is the velocity (\( \text{cm}^3/(\text{cm}^2 \cdot \text{s}) \)) of water moving towards the cathode FF. If it is via vapor phase, \( v_{H_2O,gas} \) can be obtained by assuming that the water vapor follows the ideal gas law: \( p^o V^o = R T^o \). Here, at standard condition, \( p^o = 100 \text{kPa} \), \( V^o = 22414 \text{cm}^3/\text{mol} \), \( R = 8.314 \text{J/(mol} \cdot \text{K}) \), and \( T^o = 273.15 \text{K} \). The molar volume of ideal gas at a certain temperature (\( T_{cath} \)) and pressure (\( p \)) is given by

\[
V_{i,T_{cath},p} = \frac{p^o V^o}{p} \cdot \frac{T_{cath}}{T^o}
\]  

[6.13]

where \( T_{cath} \) is the cathode temperature which is a function of current density. Given the materials used in this work at 80°C FF, the temperature is related to the current density \( i \) (A/cm\(^2\)) by \( T_{cath} = 353.15 + (i/1.5) \times 6 \), where \( T \) is in °K. The pressure is the total pressure at each RH as described in the experimental section. The \( v_{H_2O,gas} \) at each condition can be estimated by

\[
v_{H_2O,gas} = N_{H_2O,FF-CL,cath} \cdot V_{i,T,p}
\]  

[6.14]

Figure 6.5 shows the calculated \( v_{H_2O,gas} \) as a function of current density at 25%, 50%, and 75%RH. \( v_{H_2O,gas} \) increases with increasing current density at a given RH, and decreases with increasing RH at a given current density. The water leaves the cathode to the cathode FF via the DM, creating a bulk flow while the O\(_2\) diffuses in the opposite direction towards the cathode. The diffusion velocity of O\(_2\) in the water is estimated by

\[
v_{O_2-H_2O,gas} = D_{O_2-H_2O,gas} / \delta_{DM,an}
\]  

[6.15]
where \( D_{O_2-H_2O,\text{gas}} \) is 0.12 cm\(^2\)/s determined by Equation 6.7c, and \( \delta_{\text{DM,an}} \) is 176\( \mu \)m. Thus the \( v_{O_2-H_2O,\text{gas}} \) is 6.8 cm/s, which is much higher than the \( v_{H_2O,\text{gas}} \) shown in Figure 6.5. This implies that there is no problem for \( O_2 \) diffusion towards the cathode even when water vapor is moving towards the FF in the opposite direction.

Similar analysis is done for the case when the water in the DM is in a liquid form. The superficial velocity \( v_{H_2O,\text{liq}} \) now can be determined by the right side of Equation 6.14 with \( V_{i,T,P} = 18\text{cm}^3/\text{mol} \). The obtained liquid velocities are plotted in Figure 6.5. For \( O_2 \), \( D_{O_2-H_2O,\text{liq}} \) is \( \sim 10^{-5} \text{cm}^2/\text{s} \), thus the diffusive velocity is \( v_{O_2-H_2O,\text{liq}} = 5.7 \times 10^{-4} \text{cm/s} \), in the same magnitude as \( v_{H_2O,\text{liq}} \). Under this situation, the ORR kinetics might be limited by the ability of DM to remove liquid water. Flooding might occur when the DM is ineffective in removing liquid water. However, whether water leaves the DM as liquid or vapor remains an open question.
Figure 6.5: Velocity of water transported to cathode FF via vapor or liquid at 80°C, 75%, 50%, and 25%RH, respectively.

6.3.1.3 Model and Data Comparison

Having the model available for the prediction of the local RH in an operating cell, it is important to check its validity. Due to the difficulty in measuring cathode proton resistance in a H₂/O₂ cell, a better parameter that can be used as an indicator is the membrane resistance. The membrane resistance is included in the high frequency resistance (HFR), which can be measured by AC impedance and obtained by extrapolating the high frequency end of the Nyquist spectrum to the real axis, as shown in Figure 2.4 or 3.1. Following the subtraction of the electronic resistance (0.025Ω·cm²) from the HFR, the average membrane resistance ($R_{\text{mem}}$) is determined as a function of current density at each RH.

Figure 6.6 shows the average proton resistance in the membrane of a H₂/O₂ cell,
$R_{\text{mem}}$, at various current densities and channel RH levels. The $R_{\text{mem}}$ measured in H$_2$/N$_2$ as a function of RH is also included in the plot as reference. Because there’s no water production involved, an accurate correlation indicated by the dotted line between $R_{\text{mem}}$ and RH can be obtained and described by

$$R_{\text{mem}} = 42.553 \times (RH\%)^{-1.701} \quad [6.16]$$

Comparing the $R_{\text{mem}}$ measured in H$_2$/O$_2$ with the correlation curve at certain FF RH shows that up to 0.1A/cm$^2$, water production in the cathode has no influence on the membrane average RH. In other words, the RH gradient between membrane and FF is negligible. At higher current densities, there is noticeable RH difference between the membrane and the FF, especially at RH<50% condition. It should be noted that data points at 122%RH are placed at 100%RH because thermodynamically RH values over 100% are equivalent to 100%RH.
Using the parameters listed in Table 6.1 and Equations 6.1-6.11, and 6.16, the membrane resistances ($R_{\text{mem}}$) are predicted; each is the averaged value of the five control volumes. They are compared with the experimentally determined $R_{\text{mem}}$ and are shown in Figure 6.7. The comparison shows a good agreement between the measured data and the model-predicted values at all four RHs, validating the 1-D model. In what follows, the cell performance is estimated based on the predicted water profile, and compared with measured cell voltage at various conditions.
Figure 6.7: Comparison of experimentally determined average membrane resistance with model predicted values at various current densities at 80°C and at 25%, 35%, 50% and 75%RH.

6.3.2 H₂/O₂ Cell Performance

For a H₂/O₂ fuel cell, the theoretical cell voltage at zero current is the reversible cell voltage ($E_{\text{rev}}$). In reality, once current is applied, several voltage drops occur. To optimize cell performance and improve durability, it is necessary to identify the voltage losses and to quantify each term. The cell voltage ($E_{\text{cell}}$) under load is given by subtracting each loss term from the theoretical cell voltage. In this section, a cell performance model is firstly introduced considering all possible loss terms. The model predictions in H₂/O₂ cells are compared to the measured values then.
6.3.2.1 Voltage Loss Terms

Generally, H₂/Air cell performance can be described by

\[ E_{\text{cell}} = E_{\text{rev}} - i \cdot HFR - \eta_{\text{ORR}} - \eta_{\text{HOR}} - \eta_s \cdot (R_{H^+, \text{cath}}^{\text{eff}} + R_{H^+, \text{an}}^{\text{eff}}) - \eta_{\text{ir}} \]  \hspace{1cm} [6.17]

The \( HFR \) term determined by AC impedance includes the proton resistance in the membrane (\( R_{\text{mem}} \)) and electronic resistance \( R_{\text{electronic}} \) (mainly from the contact resistance between the DM and the FF). The \( \eta_{\text{ORR}} \) is the voltage loss due to the ORR kinetics, which strongly depends on the catalyst activity and is a key voltage loss in the cell performance. It is expressed by\(^{21}\)

\[ \eta_{\text{ORR}} = \frac{2.303RT}{\alpha_c F} \log \left( \frac{i + i_s}{10L_{Pt, \text{cath}} \cdot A_{Pt, \text{el}} \cdot i_{o,s}^* \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^\gamma} \right) \]  \hspace{1cm} [6.18]

where \( \alpha_c \) is the cathodic transfer coefficient with a determined value of, \( \alpha_c = 1 \),\(^{21}\) \( i_s \) is the H₂ crossover current in unit of A/cm², \( L_{Pt, \text{cath}} \) (mgPt/cm²) is the cathode Pt loading, \( A_{Pt, \text{el}} \) (m²Pt/gPt) is the electrochemical available Pt surface area, \( i_{o,s}^* \) (A/cm²Pt) is the catalyst-specific exchange current density normalized to reference oxygen partial pressure (\( p_{O_2}^* \)) of 101.3 kPa at the reference temperature (\( T^* \)) of 80°C, and \( \gamma \) (0.54)\(^{21}\) is the kinetic reaction order with respect to oxygen partial pressure.

The fourth term, \( \eta_{\text{HOR}} \), is the voltage loss caused by the hydrogen oxidation reaction (HOR) kinetics,\(^{22}\) which is usually negligible unless drawing large current densities at very dry condition and at low temperature during a freeze startup.\(^{6,23}\) Due to the fast
HOR kinetics, the $\eta_{\text{HOR}}$ follows the linear kinetics up to $\sim500\text{A/mgPt}$, as described by

$$\eta_{\text{HOR}} = i \times R_{K,\text{HOR}}$$  \[6.19\]

Where the kinetic resistance for HOR is given by

$$R_{K,\text{HOR}} = \frac{RT}{2F \cdot 10 \cdot L_{\text{Pt,an}} \cdot A_{\text{Pt,el}} \cdot i_{o,\text{HOR}(T,P_{H_2})}}$$  \[6.20\]

Equations 6.19 and 6.20 are derived from the linearization of the Butler-Volmer equation. $L_{\text{Pt,an}}$ (mgPt/cm$^2$) is the anode Pt loading, and $i_{o,\text{HOR}(T,P_{H_2})}$ (A/cm$^2$ Pt) is the exchange current density for the HOR. Its dependence on the temperature and H$_2$ partial pressure can be expressed by

$$i_{o,\text{HOR}(T,P_{H_2})} = i^*_{o,\text{HOR}} \left( \frac{P_{H_2}}{P^*_{H_2}} \right)^{\gamma_{H_2}} \exp \left[ -\frac{E_{\text{HOR}}}{RT} \left( 1 - \frac{T}{T^*} \right) \right]$$  \[6.21\]

where $i^*_{o,\text{HOR}}$ (A/cm$^2$ Pt) is the HOR exchange current density normalized to the reference temperature ($T^*$) of 80°C (353K) and reference H$_2$ partial pressure ($P^*_{H_2}$) of 101.3kPa. $E_{\text{HOR}}^{\text{rev}}$ is the activation energy of the HOR at reversible cell potential. Here, the measurement is conducted at 80°C so $E_{\text{HOR}}^{\text{rev}}$ is not necessarily needed. $\gamma_{H_2}$ is the reaction order for HOR, and a unity is used in this work based on the a dual-pathway model.

The two terms in the parenthesis, $R_{H^+,\text{cath}}^{\text{eff}}$ and $R_{H^+,\text{an}}^{\text{eff}}$ are the effective proton resistance in the cathode and the anode, respectively, both depend on the current density distribution in the electrode. $\eta_{tx}$ is the transport loss that mainly comes from the resistance...
to O₂ transport from the cathode FF to the cathode CL. For cell operated with pure O₂ on cathode, this term is negligible.

To predict the cell performance, each term in Equation 6.17 needs to be quantified based on the materials chemical-physical properties and local conditions such as temperature and RH in an electrode. The details to determine $E_{rev}$, $HFR$, and $\eta_{ORR}$ have already been discussed in Chapter 2. Here, more information is presented to estimate $R_{H^+,cath}^{eff}$, $\eta_{HOR}$, and $R_{H^+,an}^{eff}$. The $R_{H^+,cath}^{eff}$ is defined as

$$R_{H^+,cath}^{eff} = \frac{R_{H^+,cath}}{3 + \zeta}$$  \hspace{1cm} [6.22]

where $\zeta$ is a correction factor for reduced cathode utilization, and it is a function of $TS R_{H^+,cath}^{+}$. Here, TS is the Tafel slope in units of V/dec. $R_{H^+,cath}$ is the electrode proton resistance through the entire cathode thickness. To quantify the voltage loss by the cathode proton resistance, it is desired to directly measure $R_{H^+,cath}$ by AC impedance in an operating cell. Some methods have been reported to determine the voltage losses due to the proton transport, however, as discussed in Chapter 2, the AC impedance spectra obtained in H₂/O₂ cells are complicated by the contributions from both the ORR charge transfer resistance and the variation of the electrode capacitance in the O₂-cathode potential region of ~0.6 to ~1V (see Figure 2.3 in Chapter 2). This makes it very difficult, if not impossible, to quantify $R_{H^+,cath}$ properly from AC impedance measurements in H₂/O₂ cells; therefore, it makes more sense to use the $R_{H^+,cath}$ correlations with respect to ionomer to carbon weight ratio (I/C-ratio) and relative humidity (RH) obtained in H₂/N₂ cells.
In previous chapters, the voltage loss due to the anode proton resistance \( R_{H^+,an} \) is not considered because at current density as low as 0.1A/cm\(^2\), even at 35%RH, this loss is less than 1.5mV. In this chapter, cells are tested at current density as high as 2 A/cm\(^2\) and at RH as low as 25%, which might cause substantial voltage loss by the proton transport in the anode. Based on conservation of charge in the anode and negligible mass transport there, a ratio of \( R_{H^+,an} \) over \( R_{H^+,an}^{\text{eff}} \) is expressed by\(^{6,23}\)

\[
\frac{R_{H^+,an}}{R_{H^+,an}^{\text{eff}}} = \frac{\beta}{\left( e^{\beta} + e^{-\beta} \right)} \rightarrow \begin{cases} 
\beta & \text{as } \beta \to \infty \\
3 & \text{as } \beta \to 0
\end{cases}
\]

[6.23]

where \( \beta \) is the square root of resistance ratio of anode proton transport to HOR charge transfer (\( R_{K,HOR} \), as shown in Equation 6.20)\(^{6,23}\)

\[
\beta = \left( \frac{R_{H^+,an}}{R_{K,HOR}} \right)^{1/2}
\]

[6.24]

\( R_{H^+,an} \) can be evaluated using the same method for \( R_{H^+,cath} \) using a H\(_2\)/N\(_2\) cell. In this work, the \( R_{H^+,an} \) and the \( R_{H^+,cath} \) are identical because the anode and the cathode are made of the same electrodes.

As mentioned before because it is difficult to measure \( R_{H^+,cath} \) in an operating cell, there are no directly measured \( R_{H^+,cath} \) data corresponding to the predicted RH. With the validation of the water transport model by the measured membrane resistance, it is believed that the predicted RHs in the electrodes are also reliable. Since a correlation between \( R_{H^+,cath} \) and RH is known, the former could consequently be obtained based on
the predicted local electrode RH. The correlation, shown in Figure 6.8 and presented by the dashed curve, is established based on the data obtained using AC impedance in H₂/N₂ cells as a function of RH. The obtained Nyquist spectra are analyzed by the method developed in Chapter 2. The anode and cathode are made of the same electrode, so \( R_{H^+} \), \( \text{cath} \) is applicable for both the anode and the cathode. In later sections, \( R_{H^+,an} \) and \( R_{H^+,cath} \) are estimated based on the results described by

\[
R_{H^+,cath} = 9309.2 \times (RH\%)^{-2.735}
\]  

[6.25]
$y = 9309.2x^{2.73}$

$R^2 = 0.97$

**Figure 6.8:** Electrode proton resistance as a function of relative humidity in H$_2$/N$_2$ cells at 80°C, 300kPa$_{abs}$ for electrode at I/C=0.8 with 50%Pt/V catalyst and DE2021® ionomer. Data points at 122%RH are placed at 100%RH due to the fact that RH values above 100% are thermodynamically equivalent to 100%RH. Dashed line represents the correlation obtained from the measured data.

### 6.3.2.2 Comparison of Model and Experiment Cell Performance

Having all the loss terms available, the cell performance is estimated using Equations 6.17-6.25. The operating conditions are described in the experimental section (6.2). The required HOR/ORR kinetics and proton transport correlations with RH as well as the water transport parameter values/equations are listed in Table 6.2.
Table 6.2: Kinetics and transport parameter values/equations required for cell performance prediction and the 1-D water fundamental transport model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value or Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kinetics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exchange current density</td>
<td>A/cm²ₚt</td>
<td>0.3/2.1×10⁻⁸</td>
</tr>
<tr>
<td>Specific area of Pt</td>
<td>electrolyte interface</td>
<td>m²/gₚt</td>
</tr>
<tr>
<td>Anode/cathode Pt loading</td>
<td>mgₚt/cm²</td>
<td>0.4/0.4</td>
</tr>
<tr>
<td><strong>Proton conduction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane resistance at 80°C</td>
<td>Ω·cm²</td>
<td>a 42.553 × (RH%)⁻¹.⁷₀¹</td>
</tr>
<tr>
<td>Electrode proton resistance at 80°C</td>
<td>Ω·cm²</td>
<td>b 9309.2 × (RH%)⁻².⁷₂₃</td>
</tr>
<tr>
<td>Activation energy⁶</td>
<td>kJ/mol</td>
<td>6</td>
</tr>
<tr>
<td><strong>Water transport</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electro-osmotic drag coefficient</td>
<td>molH₂O/molH⁺</td>
<td>1</td>
</tr>
<tr>
<td>Water content at 30°C≤T≤95°C</td>
<td>molH₂O/molSO₃H</td>
<td>(1+0.2352((T-30)/30)RH²)(14.22RH³-18.92RH²+13.41RH), 0.1≤RH≤0.8</td>
</tr>
<tr>
<td>Water diffusivity in membrane at 80°C</td>
<td>10⁻⁶ cm²/s</td>
<td>3.327λ[-1+1.619 exp(-0.000935λ)], λ≤4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1λ[1+70 exp(-0.3λ)], λ&gt;4.4</td>
</tr>
<tr>
<td><strong>Cathode temperature⁶</strong></td>
<td>°C</td>
<td>Tᵋᵣₑₓ=80+(i/1.5)×6, i is the current density (A/cm²)</td>
</tr>
<tr>
<td><strong>Electronic resistance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFR-Rₘₑₙ</td>
<td>Ω·cm²</td>
<td>0.025</td>
</tr>
</tbody>
</table>

⁶ obtained from Figure 6.6
⁷ obtained from Figure 6.8
⁸ GM in-house measurement by Dr. Annette M Brenner

Figure 6.9 shows a comparison of cell performance between the measured and model-predicted values at 75%, 50%, 35% and 25%RH and at current densities ranging from
0.05 to 2A/cm². The symbols represent the experimental data, while the curves are plotted based on the model.

**Figure 6.9**: Comparison of measured cell voltage with the predicted. Lines represent model predicted performance, and symbols represent measured values at the corresponding condition at 80°C with H₂/O₂ (3500/3500 sccm) feeds on the anode and cathode, respectively. $p_{\text{H}_2, \text{FF}}=p_{\text{O}_2, \text{FF}}=253$ kPa.

The difference between the predicted and measured cell performance ($E_{\text{predicted}} - E_{\text{measured}}$) is plotted in Figure 6.10. The prediction agrees with the experimental data very well for channel RH of 75% and 50%, where the difference is within 14mV at all current densities. For 35%RH, the difference is less than 20mV; at 25%RH, the difference varies no more than 25mV at all current densities. The predicted cell performance is more than 10mV higher than the measured voltage at dry conditions when the current density is above 0.6A/cm², indicating that some loss terms might be underestimated in the current model. One possible reason is that the ORR kinetics used in the model does not account
for the effect of RH. There are ~25 mV loss observed at 35%RH for electrodes with I/C-ratios ranging from 0.4 to 1.2.\textsuperscript{2} Another possibility is that the predicted cathode RH is too high; consequently the accounted cathode proton transport loss is lower than the actual value. The accuracy of the local RH in the cathode depends on the reliability of the measured water and thermal transport parameter values. In the next section, the effect of the measured transport parameter variation on the cell performance is discussed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_10.png}
\caption{Voltage difference between model-predicted and measured cell voltages ($E_{\text{predicted}} - E_{\text{measured}}$).}
\end{figure}

6.3.3 Effect of Transport Parameter Variation on the Cell Performance

Among the input parameters for the 1-D water transport model, the water diffusivity in the membrane, $D_{H_2O,\text{mem}}$, and the temperature difference between the cathode and FF are measured in-house. Here, the effect of the accuracy of these two parameters on the cell performance is discussed by inspecting two examples: 50%RH 2A/cm\textsuperscript{2} and 25%RH...
and 2A/cm². Figure 6.11 shows that varying $D_{H_2O,\text{mem}}$ by ±20% away from the applied value calculated by Equation 6.9, the error in the cell voltage is 5±5mV at 50%RH, and 9±1mV at 25%RH. This indicates that even 20% error in $D_{H_2O,\text{mem}}$ cannot account for all the difference between the estimated and measured cell voltage under dry conditions.

**Figure 6.11**: Variation of Cell performance with assumed changes in water diffusion coefficient in membrane, at 2A/cm², 80°C FF temperature, and 25%RH and 50%RH, respectively. The dashed line represents the measured cell voltage (0.548V) at 25%RH. The dash-dotted line represents the cell voltage (0.639V) at 50%RH.

The effect of assumed variations in $D_{H_2O,\text{mem}}$ on the local RH in the membrane and the electrodes and on their effective resistances with the variations of $D_{H_2O,\text{mem}}$ are shown in Table 6.3. It shows that the effective proton resistances in the anode and the cathode are changing in the opposite directions and the amount of changes are almost identical, resulting in very slight cell performance variation by varying the $D_{H_2O,\text{mem}}$. At both conditions, the entire cathode local RHs are beyond 80%, where the electrode proton
resistance only slightly changes with RH, as shown in Figure 6.8. For the membrane, at 50%RH, the RHs are above 65%RH, where the $R_{\text{mem}}$ weakly depends on the RH, as shown in Figure 6.6. Though at 25%RH, the membrane RHs are below 50%, where $R_{\text{mem}}$ strongly depends on RH, there is little change in RH with the assumed variation in $D_{\text{H}_2\text{O,mem}}$. An interesting result as shown in Table 6.3 is that at dry condition, the anode proton resistance is substantial. It can cause ~40mV voltage loss at 2A/cm$^2$, so it has to be considered at dry conditions and high current densities.

**Table 6.3**: Local RH at 2A/cm$^2$, 50%RH and 25%RH, respectively, in the membrane, the anode, and the cathode as well as their corresponding effective resistance at various water diffusivities. The applied $D_{\text{H}_2\text{O,mem}}$ is calculated by Equation 6.9.

<table>
<thead>
<tr>
<th>Channel RH%</th>
<th>Variation of $D_{\text{H}_2\text{O,mem}}$</th>
<th>Local RH%</th>
<th>Resistance (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>An</td>
<td>Cath</td>
</tr>
<tr>
<td>50</td>
<td>-20%</td>
<td>38.9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Applied</td>
<td>41.5</td>
<td>96.2</td>
</tr>
<tr>
<td></td>
<td>+20%</td>
<td>43.3</td>
<td>90.9</td>
</tr>
<tr>
<td>25</td>
<td>-20%</td>
<td>17.3</td>
<td>92.9</td>
</tr>
<tr>
<td></td>
<td>Applied</td>
<td>19.6</td>
<td>85.9</td>
</tr>
<tr>
<td></td>
<td>+20%</td>
<td>21.3</td>
<td>80.8</td>
</tr>
</tbody>
</table>

The temperature gradient between the cathode and the FF, $\Delta T_{\text{CL-FF,cath}}$, is determined as 6°C at 1.5A/cm$^2$, which is proportional to the applied current density: higher applied current density results in higher $\Delta T_{\text{CL-FF,cath}}$. Figure 6.12 demonstrates the changes in the predicted cell voltage with the assumed variation of this temperature difference at 1.5A/cm$^2$. It shows that at 25%RH for every one degree temperature increase or decrease, the predicted cell voltage correspondingly decreases or increases by 17mV compared to
the performance obtained using the applied $\Delta T_{\text{CL-FF,cath}}$ (6°C at 1.5A/cm$^2$). While at 50%RH, less than 8mV/°C variation is observed. Therefore, the accuracy of measured thermal conductivity is of more important for the cell performance prediction at very low RH, i.e., 25%, than at higher RH. Nevertheless, no clear conclusion can be drawn from the comparison and it appears unlikely that the large difference ($E_{\text{predicted}} - E_{\text{measured}}$) at 25%RH is attributed to the accuracy of the measured thermal properties. There might be some unknown sources causing the extra performance loss than expected.

![Figure 6.12: Variation of Cell performance with changes in temperature gradient between cathode and FF, at 2A/cm$^2$, 80°C FF temperature, and 25%RH and 50%RH, respectively. The dashed line represents the measured cell voltage (0.548V) at 25%RH. The dash-dotted line represents the cell voltage (0.639V) at 50%RH.](image)

Table 6.4 shows the local RH changes with the temperature gradient $\Delta T_{\text{CL-FF,cath}}$ in membrane and electrodes, at 50% and 25% channel RH. The corresponding proton resistance in each component is also listed in the table.
Table 6.4 shows that the effective proton resistance of the anode and the cathode are changing in the same direction. Again, at 50% channel RH, the anode effective proton resistance is 1/4-1/3 of the cathode proton resistance, while at 25%RH it is comparable to the cathode resistance, so it has to be considered. Due to the same reason stated before, all cathode local RHs lie in the range where they have little effect on the proton resistance, so their changes are very small. As shown in the table, the membrane RH increases with decreasing $\Delta T_{\text{CL-FF,cath}}$ by ~2.5 RH-points/°C at both conditions. However, at 25%RH, the change in membrane resistance doubles the changes at 50%RH due to its
strong RH dependence below 60%. This explains the results shown in Figure 6.12 where cell voltage changes more with changing $\Delta T_{\text{CL-FF,cath}}$ at 25%RH than at 50%RH, again due to the strong dependence of the membrane resistance on the RH.

Another important observation shown in Tables 6.3 and 6.4 is that the cathode local RH is over 80% even at 25% channel RH. This implies that at 2A/cm$^2$, and at dry condition the RH effect on the ORR kinetics might be minor.$^4$ However, this depends on the accuracy of the predicted cathode RH. The large difference in cell voltage between the predicted and the measured voltage at dry condition might come from unknown sources.

6.3.4 Evaluation of Local RH from Measured Cell Voltage

The previous section describes a 1-D water transport model which predicts the local RH in the membrane and the electrodes. However, only the membrane resistance could be used to validate the model. In this section, an approach is presented to extract the cathode proton resistance based on the measured cell voltage, from which and subsequently the RH is determined based on Equation 6.25. Finally, the obtained RH is compared with what is predicted by the water transport model.

The voltage loss due to proton conduction in the electrode is approximately equal to the kinetic voltage ($E_{\text{kinetics}}$) minus the cell voltage after HFR correction ($E_{\text{HFR-free}}$). In Equation 6.17, the $\eta_{\text{HOR}}$ is negligible due to its fast kinetics at the current operating condition, and $\eta_{\text{cx}}$ is also negligible (less than 3mV in this work). Rearranging Equation 6.17 gives
\[
i \cdot (R_{H^+,an}^{\text{eff}} + R_{H^+,cath}^{\text{eff}}) = (E_{\text{rev}} - \eta_{\text{ORR}}) - (E_{\text{cell}} + i \cdot HFR) \equiv E_{\text{kinetics}} - E_{\text{HFR-free}}
\]  

[6.26]

Figure 6.13 shows the scheme of this approach.

![Schematic of the difference between HFR corrected cell voltage and polarization curve subtracted by ORR kinetics.](image)

**Figure 6.13:** Schematic of the difference between HFR corrected cell voltage and polarization curve subtracted by ORR kinetics.

The \( E_{\text{kinetics}} \) is defined as

\[
E_{\text{kinetics}} = E_{\text{ref}} - TS \log \frac{i}{i_{\text{ref}}}
\]

[6.27]

where \( E_{\text{ref}} \) is the voltage at fully humidified conditions and at the reference current density \( i_{\text{ref}} \), \( TS \) is the Tafel slope (0.07V/dec at 80 °C), and \( i \) is the applied current density.
Here, 0.9V \( (E_{cell} + iHFR) \) at fully humidified condition is selected as the reference voltage. Consequently, the corresponding current density is \( i_{ref} \) (i.e., \( i + i_x \)), which is 0.112A/cm\(^2\) as shown in Figure 6.14. \( i_x \) is the additional ORR current density caused by H\(_2\) crossover from the anode to the cathode. A value of 1.5mA/cm\(^2\) is applied for the \( i_x \) in Figure 6.14. It should be noticed that the \( E_{kinetics} \) used in this work is assumed to be RH independent and varies only with current density.

![Graph](image)

**Figure 6.14**: Polarization curve and reference current density at reference voltage (0.9V) at 122%RH, 80°C in H\(_2\)/O\(_2\).

Having the \( E_{kinetics} \) and HFR-corrected voltages available, the losses induced by proton conduction in the electrode on the right side of Equation 6.26 can be determined.
If the losses caused by proton conduction in the anode are subtracted from the total proton conduction losses in the electrodes, the remainder is due to the cathode proton conduction. In previous chapters, the voltage losses caused by proton transport in anode were neglected when operating at low current density (0.1A/cm²) and moderately dry conditions (RH ≥ 35%). Here, the cell are tested at current density as high as 2 A/cm² and at RH as low as 25%, which might require proton transport further into the anode. Under this circumstance, the voltage loss from the anode proton conduction becomes substantial, as shown in Tables 6.3 and 6.4. The proton resistance in the anode through the entire catalyst layer is shown in Figure 6.8 as a function of RH. $R'_{an}$ is quantified by Equations 6.19-6.21 and 6.23-6.24.

Once $R'_{an}$ at each condition is obtained, the corresponding voltage loss ($i \cdot R'_{cath}$) in the cathode could be isolated from the other losses. In order to get $R'_{cath}$, Equation 6.22 needs to be solved iteratively. The details of the correlation between $\zeta$ and $R'_{cath}$ were described in Ref. 3. After obtaining $R'_{cath}$, the RH can be obtained from the dependence of the cathode proton resistance on the RH, as shown in Figure 6.8. The obtained RH is compared with the model-predicted RH in the cathode, and is plotted in Figure 6.15. The dashed 45° line represents perfect agreement.
Figure 6.15: Comparison of experimentally determined RH in cathode with the 1-D model predicted RH values at 75%, 50%, 35% and 25% FF channel RH at 80°C and various current densities with H₂/O₂ feeds (3500/3500 sccm) on the anode and cathode respectively.

Figure 6.15 shows that consistently the predicted RH values in the cathode are higher than the ones derived by experimental data. In other words, the cathode proton resistance is underestimated by the model, thus the model-predicted cell voltage is higher than the measured voltage. This is consistent with the results shown in Figure 6.9. The discrepancy between the local RH in the cathode, as shown in Figure 6.15, implies that there are additional voltage losses, warranting further research. The unknown voltage losses can be identified by controlled experiments, particularly at low RH and high current density conditions. Clearly, the accuracy of this approach greatly depends on whether or not ORR kinetics is indeed independent of the RH and Pt surface status (Pt surface oxide coverage), as has been previously assumed in the performance model.
6.4 SUMMARY

A 1-D model based on water transport is presented, describing the local RH distribution in the membrane and the electrodes under various conditions. The predicted RH distribution was validated by two methods: Comparison of the experimental membrane resistance to that predicted by the model; Comparison of the experimentally measured cell voltage to that predicted by the cell performance model. Both comparisons gave good agreement although the model overpredicts the cell voltage at low RH and high current density. The discrepancy in local RH obtained from the two approaches implies the possible existence of additional voltage losses unaccounted for by the model. Possible reasons causing this discrepancy are investigated by an error analysis of the transport parameters.

The validated water transport model allows the prediction of undesirable dryout and liquid water formation in the electrodes. Furthermore it allows one to predict the water fluxes toward the anode and the cathode’s FF and their dependence on operating conditions. The ability of the DM in removing liquid water is critical to avoid flooding and O₂ diffusion limitations. Future work is needed to improve the ORR kinetics and identify additional voltage loss terms.

**SYMBOLS**

\[ A_{Pt,el} \] \text{electrochemical available Pt surface area, m}^2_\text{Pt/gPt} \\
\[ E_{cell} \] \text{cell voltage, V} \\
\[ E_{HFR-free} \] \text{cell voltage plus corrections from high frequency resistance, V} \\
\[ E_{kinetics} \] \text{cell voltage}
$E_{\text{ref}}$ reference potential ($E_{\text{kinetics}}$-$E_{\text{HFR-free}}$) at 122%RH, 0.9V

$E_{\text{rev}}$ reversible cell potential (function of T, $P_{H_2}$, $P_{O_2}$, RH), V

$F$ Faraday constant, A·s/equiv

$f_{H_2O}$ fraction of product water transported to cathode flow-field

$i$ current density, A/cm$^2$

$i_{o,HOR}$ exchange current density for HOR, A/cm$^2_{\text{Pt}}$

$i_{o,HOR(T,P_{H_2})}$ exchange current density for the HOR as a function of temperature and H$_2$ partial pressure, A/cm$^2_{\text{Pt}}$

$i_{o,HOR}^*$ exchange current density for HOR normalized to reference temperature of 80°C and reference H$_2$ partial pressure of 101.3 kPa, A/cm$^2_{\text{Pt}}$

$i_{o,s}^*$ exchange current density referenced to 80°C and 101.3 kPa of oxygen partial pressure, based on Pt surface area, A/cm$^2_{\text{Pt}}$

$i_{\text{ref}}$ current density at $E_{\text{ref}}$, A/cm$^2$

$i_x$ ORR current density associated with H$_2$ crossover from anode to cathode, A/cm$^2$

$L_{\text{Pt,an}}$ anode Pt loading, mg$_{\text{Pt}}$/cm$^2$

$L_{\text{Pt,cath}}$ cathode Pt loading, mg$_{\text{Pt}}$/cm$^2$

$P_{H_2}$ H$_2$ partial pressure, kPa

$P_{H_2}^*$ reference H$_2$ partial pressure, 101.3 kPa

$P^*$ standard pressure, 100 kPa

$P_{O_2}$ O$_2$ partial pressure, kPa

$P_{O_2}^*$ reference O$_2$ partial pressure, 101.3 kPa

$q$ heat flux, W/cm$^2$

$R_{\text{electronic}}$ electronic resistance of the cell, Ω·cm$^2$

$R_{H^+,an}$ anode proton resistance, Ω·cm$^2$

$R_{H^+,cath}$ cathode proton resistance, Ω·cm$^2$

$R_{\text{eff}}^*_{H^+,an}$ effective proton resistance in the anode, Ω·cm$^2$

$R_{\text{eff}}^*_{H^+,cath}$ effective proton resistance in the cathode, Ω·cm$^2$

$R_{K,HOR}$ kinetic resistance of HOR, Ω·cm$^2$

$R_{\text{mem}}$ average membrane resistance, Ω·cm$^2$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{T,\text{mem}}$</td>
<td>thermal resistance in membrane, cm²·K/W</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K or °C</td>
</tr>
<tr>
<td>$T^o$</td>
<td>standard temperature, 0 °C</td>
</tr>
<tr>
<td>$T^*$</td>
<td>reference temperature, 80°C or 353 K</td>
</tr>
<tr>
<td>$v_{\text{H}_2\text{O,\text{gas}}}$</td>
<td>velocity of gaseous water towards the cathode FF, cm/s</td>
</tr>
<tr>
<td>$v_{\text{H}_2\text{O,\text{liq}}}$</td>
<td>velocity of liquid water towards the cathode FF, cm/s</td>
</tr>
<tr>
<td>$V_{i,T,p}$</td>
<td>ideal gas molar volume as a function of current temperature and pressure, cm³/mol</td>
</tr>
<tr>
<td>$V^o$</td>
<td>ideal gas molar volume at standard condition, 22414 cm³/mol</td>
</tr>
<tr>
<td>$v_{O_2-\text{H}_2\text{O,\text{gas}}}$</td>
<td>velocity of O₂ diffusion in gaseous water, cm/s</td>
</tr>
<tr>
<td>$v_{O_2-\text{H}_2\text{O,\text{liq}}}$</td>
<td>velocity of O₂ diffusion in liquid water, cm/s</td>
</tr>
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</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_c$</td>
<td>cathode transfer coefficient</td>
</tr>
<tr>
<td>$\beta$</td>
<td>square root of the resistance ratio of anode proton conduction to HOR charge transfer</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>porosity</td>
</tr>
<tr>
<td>$\eta_{\text{HOR}}$</td>
<td>overpotential of the HOR, V</td>
</tr>
<tr>
<td>$\eta_{\text{ORR}}$</td>
<td>overpotential of the ORR, V</td>
</tr>
<tr>
<td>$\eta_{\text{tr}}$</td>
<td>transport loss, V</td>
</tr>
<tr>
<td>$\gamma_{\text{H}_2}$</td>
<td>reaction order for HOR</td>
</tr>
<tr>
<td>$\gamma_{O_2}$</td>
<td>reaction order for ORR</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>water content, molH₂O/molSO₃H</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>diffusion volume of species $i$, cm³/g-mol</td>
</tr>
<tr>
<td>$\rho_{H^+,\text{an}}$</td>
<td>proton resistivity in the anode, Ω·cm</td>
</tr>
<tr>
<td>$\rho_{H^+,\text{cath}}$</td>
<td>proton resistivity in the cathode, Ω·cm</td>
</tr>
<tr>
<td>$\rho_{H^+,\text{electrode}}$</td>
<td>proton resistivity in the electrode, Ω·cm</td>
</tr>
<tr>
<td>$\tau$</td>
<td>tortuosity</td>
</tr>
<tr>
<td>$\xi$</td>
<td>electro-osmotic drag coefficient, molH₂O/molH⁺</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>correction factor for reduced cathode proton transport length to membrane</td>
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REFERENCES


Chapter 7

Measurement of Platinum Oxide Coverage in a Proton Exchange Membrane Fuel Cell

7.1 INTRODUCTION

In proton exchange membrane (PEM) fuel cells, the oxygen reduction reaction (ORR) occurs in a potential range where the platinum (Pt) surface is partially oxidized. ORR kinetic expressions have been developed that are both engineering\textsuperscript{1-4} and mechanistic\textsuperscript{5-7} in form, the latter are characterized by attempts to explicitly consider the role of Pt oxide, which itself can exist in a variety of forms (e.g. OH, O, strongly or weakly bonded). These oxides can be formed either from water or gas phase oxygen and affect the ORR reaction rate primarily as intermediates\textsuperscript{5,6} or poisons\textsuperscript{8,9}. Furthermore, the formation and reduction of Pt oxide are known to be very sluggish and perhaps irreversible\textsuperscript{10,11} Darling and Meyers proposed a kinetics model for the Pt dissolution in PEM fuel cell where 3 reactions consist of the Pt dissolution.\textsuperscript{12} It is thus not surprising that detailed mechanisms for ORR reaction are still a fertile research area, since the surface state under operation is poorly understood. In-situ X-Ray Absorption Spectroscopy (XAS)\textsuperscript{13,14} and ex-situ X-Ray Photoelectron Spectroscopy (XPS)\textsuperscript{15} allow the study of the oxide as a function of potential, but further work is needed to establish these as species-specific (e.g. O vs. OH) and quantitative techniques.
As a limiting case, the system can be simplified by removing the O\textsubscript{2} and studying only the equilibrium associated with H\textsubscript{2}O and potential. The Pt oxide formation thus requires water as a reactant and depends on the electrode potential:

\[
\text{Pt} + \text{H}_2\text{O} \leftrightarrow \text{PtOH} + \text{H}^+ + e^- \quad [7.1]
\]

It is assumed in this study that at potentials of $\leq 0.9\text{V}_{\text{RHE}}$ (vs. Reversible Hydrogen Electrode) that PtOH, requiring only one electron transfer, is the primary surface species. It is also possible that this reaction is followed by $\text{PtOH} + \text{H}_2\text{O} \leftrightarrow \text{Pt(OH)}_2 + \text{H}^+ + e^-$ or by $\text{PtOH} \leftrightarrow \text{PtO} + \text{H}^+ + e^-$ to form Pt(OH\textsubscript{2}) or PtO on the surface. Coulometry is used to determine the amount of charge required to reduce the Pt oxide as a function of electrode potential, as was done in earlier studies at 25°C (Paik et. al\textsuperscript{16}) and 100°C (Xu et. al\textsuperscript{17}). In those efforts, exposure to O\textsubscript{2} was observed to have a long-lasting impact on the surface oxide coverage of an electrode held at constant potential, persisting even 2.5 hours after purging the cathode with N\textsubscript{2}. This is an important result because, if true, it implies that accurate ORR kinetics would need to explicitly comprehend Pt oxide kinetics and/or electrode history, outside the scope of existing kinetics expressions, as discussed by Gottesfeld\textsuperscript{18}.

In this work, the equilibrium oxide coverage is carefully measured at 80°C from 0.6 to 0.9V\textsubscript{RHE}, under typical fuel cell electrode operating conditions. Additionally, the electrode potential is maintained at an IR-free value during the O\textsubscript{2} exposures to avoid the IR effect of the ORR large current.

This work follows a previous study\textsuperscript{19} and further confirms the zero impact of O\textsubscript{2} exposure on the irreversible Pt oxide coverage. Initially, the time dependence of the
PtOH coverage dependence is studied by measuring the charge accumulation while holding the potential constant. The Pt oxide coverage is measured at certain potentials at 80°C and fully humidified condition. The effects of relative humidity (RH) and temperature on the coverage of Pt oxide in H2/N2 cells are further investigated at various potentials. Although the measured Pt oxide is limited to that formed from H2O and includes no gas phase oxygen contribution, the method provides a lower bound of the oxide present in an operating fuel cell. Hopefully the result of this study provides some insight into the mechanism of ORR on a partially oxidized Pt surface, as well as the mechanism of Pt activity degradation due to oxide formation during ORR.

7.2 EXPERIMENTAL

Membrane Electrode Assembly (MEA)

The effects of residence time, RH, and temperature on PtOH coverage were studied in this work. The MEAs were fabricated with ~50wt.% Pt/Vulcan catalyst (TKK, Japan) and DE2020® ionomer (DuPont, USA) by hot pressing electrode decals onto 50 µm thick AK SF1102® membranes. Anode Pt loading was ~0.05mgPt/cm². Cathode Pt loadings was ~0.4 mgPt/cm² with an electrochemical active area of 40-50m²/gpt. The MEAs used in the oxygen exposure effect on PtOH coverage were made with ~50wt.% Pt/Vulcan catalyst (TKK, Japan) and DE2021® ionomer (DuPont, USA) by hot pressing electrode decals onto a 50 µm thick Nafion® membrane (DuPont, USA). Cathode and anode Pt loadings are ~0.4 mgPt/cm² with an electrochemical active area of 40-45m²/gpt. The MEA’s architecture is the same as the one used in Chapter 5 with 5cm² active areas. Unless specifically mentioned, the experiments were conducted on 50cm² cells. The anode and cathode diffusion media were SGL 25BC.
Dependence of Potential on H₂ Crossover Current

The HOR/HER (hydrogen evolution reaction) currents were collected at each held potential for 45min by stepping from the open circuit voltage (OCV) at 80°C, 100%RH. The anode gas was 100%H₂, 50%H₂, or 10%H₂ mixed with N₂. The total gas flow rate was 1000/1000 sccm on anode/cathode (N₂), and the total pressure \( p_T = 150 \text{kPa}_{\text{abs}} \). For each case, the measurements were conducted in the anodic, then cathodic directions.

Effects of RH and Temperature on H-adsorption/desorption

H-adsorption/desorption (HAD) areas were quantified by measuring CVs (0.05-0.6V \(_{\text{RHE}}\)) at temperatures from 30°C to 90°C in H₂/N₂ cells under fully saturated condition. The CVs were also collected at subsaturated conditions, 75%, 50% and 35%RH at 80°C and at the corresponding total absolute pressure of 101.3kPa plus the corresponding water vapor pressure at each RH. Namely, the total pressure, \( p_T \) is 150kPa\(_{\text{abs}}\), at 100%RH, 138kPa\(_{\text{abs}}\), at 75%RH, 126kPa\(_{\text{abs}}\), at 50%RH, and 120kPa\(_{\text{abs}}\), at 35%RH. All CVs were collected at a scan rate of 20mV/s.

Effects of Resident Time, RH and Temperature on Pt oxide Coverage

The time dependence of Pt oxide coverage is measured by changing the time of the held potential from 5sec to 120min at 0.85V and 0.9V, respectively. The RH-dependent Pt oxide coverage was measured at 80°C, 100%, 75%, 50% and 35%RH. The temperature effect on the Pt oxide coverage was tested at 30 to 90°C at fully saturated condition. Before the measurements, the cell was pre-conditioned to reach the operating conditions by flowing 10% H₂ (in N₂) through the anode and N₂ through the cathode with a flow rate of 1000 sccm on both sides. Potentials (0.565-0.865V \(_{\text{cell}}\), 0.6-0.9V \(_{\text{RHE}}\), 50 mV increments) were applied and held for 45min at the required RH and temperature.
condition. The cyclic voltammograms (CVs) (Gamry® G750) were collected by scanning negatively from the hold potential at a scan rate of 20mV/s down to 0.05V_{RHE} followed by three sweeps with potential ranging from 0.05 to 0.6V_{RHE}. The N2 flow rate was kept at 100 sccm while CVs were collected.

**Effect of O2 Exposure on Pt oxide Coverage**

Separate mass flow controllers (MFCs) and humidifiers were used for N2 and O2-containing gases, as shown in Figure 7.1. The transition from a N2 environment to an O2 environment was accomplished by switching a four-way valve, thus eliminating the problems of humidifier purge and manifold dead zone that were experienced in earlier works.16, 17, 19 The experiments were conducted on a 5cm² cell at 80°C, 150kPa_{abs}, and 100% RH.

![Figure 7.1](image-url): Experimental set-up for MFCs and humidifiers. Cathode side was equipped with two separate inlet streams and a four-way valve to minimize N₂→O₂→N₂ turnover times.
The cell was pre-conditioned for 1 hr. at open-circuit (~0.1 V\textsubscript{RHE}) in 10% H\textsubscript{2} (in N\textsubscript{2}) on the anode and N\textsubscript{2} on the cathode with a flow rate of 2000 sccm on both sides. Potentials (0.565-0.865V\textsubscript{cell}, 0.6-0.9V\textsubscript{RHE}, 50 mV increments) were applied and held for 45 min total for each case. The current was then noted, representing the H\textsubscript{2} oxidation current limited by the membrane H\textsubscript{2}-permeation rate. The maximum H\textsubscript{2}-permeation limiting current under these conditions, ~0.15 mA/cm\textsuperscript{2}, represented a small baseline correction relative to the Pt oxide reduction current during the subsequent CVs.

At the end of the 45 min potential hold, the N\textsubscript{2} flow rate was decreased to 100 sccm to minimize artifacts in the Pt-hydride region of the subsequent CV because of excessive N\textsubscript{2} flow rate on the cathode\textsuperscript{20, 21}. Two minutes later, CVs (Gamry® G750) were collected by cathodically scanning from the holding potential at 20mV/s down to 0.05V followed by three cyclic sweeps with potential ranging from 0.05 to 0.6V\textsubscript{RHE}. Integration relative to baseline was then done to quantify the charge required to reduce the oxide.

Three additional sets of experiments were also done, each involving exposure to different gas-phase O\textsubscript{2} concentration. Electrode preconditioning for 1 hr. at open circuit as described above was followed by potential hold (0.65, 0.7, 0.75, 0.8, 0.85, and 0.9V\textsubscript{RHE}) for 5 min. for each case. Then the N\textsubscript{2} was switched to 2000 sccm air, 50% O\textsubscript{2} in N\textsubscript{2}, or 100% O\textsubscript{2} (dry, concentrations prior to humidification) for 30 min while holding constant the electrode high-frequency-resistance (HFR) corrected voltage. This was done using a total cell potential control algorithm that relied on current density and 1 kHz HFR measurements; the algorithm was implemented in Labview and updated the electrode potential setpoint every second. The potential drop in the cathode electrolyte was estimated to be only 11 mV at the highest current density in pure O\textsubscript{2},\textsuperscript{22} and no correction
was made for this. After 30 min. of O₂ exposure, 2000 sccm N₂ was then switched back into the cathode compartment for 10 min. of purging, while maintaining the potential hold. Then, the N₂ flow rate was reduced to 100 sccm, and two minutes later the potential was cathodically scanned at 20 mV/sec to 0.05 Vᵣₑ₇ₑ, yielding the current signal needed to quantify the oxide reduction charge, followed by three CVs (0.05-0.6 Vᵣₑ₇ₑ).

The charge required to reduce the oxide for each experiment was converted to surface coverage assuming that the oxide comprised of PtOH and required a reduction charge of 210µC/cm²ₚₙ. The Pt surface area, needed to translate the PtOH amount to fractional coverage, was determined as the average of two PtH coverage measurements taken before and after each of the four experimental sets. This was done on the same cell but with a different test apparatus and conditions (30°C, 100%RH with 200/50 sccm H₂/N₂ flow rates, 210µC/cm²ₚₙ), to minimize experimental artifacts.²⁰, ²¹ Measured values varied from 40-45 m²/gₚₙ.

Similar results have been reported earlier from similar experiments, but in the current work diluted H₂ (10% H₂ in N₂) was used on the anode and 50µm membrane in comparison to 100% H₂ and 125µm membrane in the earlier study.¹⁹ These changes decreased membrane dryout in the low-voltage O₂ experiments while also decreased the H₂ permeation current, improving the signal-to-baseline ratio. The results reported in this work, within 20% of those reported earlier, are more accurate because of these experimental improvements.

### 7.3 RESULTS AND DISCUSSION

As mentioned in the beginning of this work, the Pt surface status depends on the
potential, RH, and temperature. Under certain conditions, residence time is also of great importance. For a fair comparison between different conditions, it is necessary to determine a reasonable equilibrium time. Another very important parameter, Pt surface charge per area for HAD, which is not directly related to Pt oxide, but provides reference charge for the oxide quantification, is required to investigate its dependence on temperature and RH. All the above mentioned subjects are addressed one by one in details later. Due to the unique properties of the proton exchange membrane, the H₂ crossover always exists, which could result in difficulty in data analysis. More details on the concerns caused by H₂ crossover on the data acquisition and analysis are discussed in section 7.3.1 prior to studying the Pt oxide formation.

7.3.1 Dependence of H₂-crossover Current on Potential

10%H₂ in N₂ was used on the anode to decrease the H₂-crossover in order to reduce the background signal error in integrating the charge passed during the voltammetric Pt oxide reduction. The reason for this is illustrated by Figure 7.2; the measurements were conducted with 100% H₂, 50%H₂ and 10% H₂ using a 50 micron membrane. Data point at each held potential is the average value of the last 10 min out of 45 min total holding time. For all three cases, the results show that the H₂-crossover current is determined by the membrane permeation rate at potential greater than 0.2V up to 0.75V; above 0.75V the current drops sharply with potential. In other words, the HOR is slowed down probably due to the presence of Pt oxide, and the reaction is kinetically controlled. Further studies are needed to investigate the HOR kinetics in the potential beyond 0.75V_{RHE}. As shown in Figure 7.2, HOR current decreases quickly with increasing potential, and when the potential approaches 1V, only <20% of the
permeation-limited current could be obtained. In the Pt oxide coverage studies, the same membrane (50μm thick) were used with 10%H₂ in N₂ on anode, lowering the H₂-permeation limited current by 10 times compared to the case with 100% H₂, which is the case for the test shown in Figure 7.2. Consequently, the approach of using diluted H₂ (10%H₂ balanced with N₂) on anode significantly decreases the background signal error by 10 times that could be introduced while integrating charges in CVs in the potential range of 0.75V_{RHE} or above. For the MEAs used in this work, the H₂-permeation limiting current density is no more than 0.15 mA/cm² at all operating conditions with 10%H₂ (in N₂) flowing on the anode.

It is a common practice to use a H₂-permeation limited current to correct the applied current density in ORR kinetics studies. The results in Figure 7.2 imply that the dependence of HOR current on potential would have to be considered if the ORR kinetics measurements were conducted at the potentials with substantial Pt oxide coverage. Furthermore, the knowledge of such dependence is essential for designing a fuel cell system that supplies H₂ into the cathode to assist cold-start, in which “H₂ slip” at cathode exit is observed at high cathode potentials.
Figure 7.2: Dependence of H$_2$-crossover current on potential at 80°C, 100%RH in a H$_2$/N$_2$, 50%H$_2$ (in N$_2$)/N$_2$, or 10%H$_2$ (in N$_2$)/N$_2$ cell. Data point at each holding potential is the average value of the last 10 min out of 45 min total holding time.

7.3.2 Effects of RH and Temperature on H-adsorption/desorption

Prior to quantifying the Pt oxide formation under various conditions, it is desired to know the available Pt surface area. A reliable method is measuring the Pt electrochemical area involved in the HAD region, which is believed to be kinetically fast and that a monolayer of Pt hydride forms. The HAD area (m$^2$/g$_{Pt}$) is determined at 30°C, 100% RH and ambient pressure as a routine electrode characterization test in small-scale testing. However, most of the fuel cell performance or durability tests were conducted at much higher temperature (i.e. 80°C) and sub-saturated conditions. Here tests were conducted to determine the RH and temperature impact on the H-adsorption/desorption
measurements. Figure 7.3a shows the CVs measured in H₂/N₂ cells at saturated conditions and temperatures from 30°C to 90°C after H₂-crossover current correction. The gas phase pressure was maintained constant (101.3 kPa) at all the tested temperatures, and all the potentials shown in the later figures have been converted to the values versus RHE₁₀₁ kPa H₂ at each temperature. Clearly, temperature has some effect on the shapes of the CVs. With increasing temperature, the characteristic HAD peaks shift to more negative potential direction, which might be due to the weakened H adsorption strength on Pt. Therefore, one might expect to see lower HAD areas with increasing temperature. However, the charge integration in the HAD region showed that HAD area is barely changed within the studied temperature range (i.e. 30 to 90°C) shown in Figure 7.3b, in which HAD was normalized by the maximum value (40 m²/gPt) among the group. A value of 210 µC/cm²Pt, which is the commonly used average charge for different Pt surfaces,²³ ²⁴ was assumed for the HAD calculation, which is expressed as

$$\text{HAD (m}^2/\text{g}_\text{Pt}) = \frac{Q(\mu\text{C/cm}^2)(0.1 \text{ m}^2/\text{cm}^2_{\text{Pt}})}{210 (\mu\text{C/cm}^2_{\text{Pt}})[\text{Pt loading (mg}_{\text{Pt}}/\text{cm}^2])] \quad [7.2]$$

where Q is the charge integrated from the area defined in Figure 7.4.
Figure 7.3: Temperature effect on H-adsorption/desorption at 100%RH and temperature from 30 to 90°C. (a): CVs and (b): Normalized HAD at various temperatures.
Figure 7.4: Illustration of H-adsorption/desorption area calculation.

The RH effect on the HAD is shown in Figure 7.5. Some variation in the peaks position with RHs was observed; peaks shift to more negative potential with decreasing RH, which is consistent with the literature. However, this change has no influence on the HAD areas if the charge is integrated in the HAD regime. These two findings will be used in the later data analysis on the effects of RH and temperature on the coverage of Pt oxide, where a constant HAD will be used in the calculations.
Figure 7.5: RH effect on H-adsorption/desorption at 80°C, 100%, 75%, 50% and 35%RH.

7.3.3 Pt Oxide Coverage

The actual Pt oxide species are not known, PtOH is used as a representative species here since it requires only one electron transfer and is the simplest form. If the coverage is greater than 1, it implies that either multilayer OH or, more likely, O (2 electrons) and then later on surface-layer oxide may form on the catalyst surface. The PtOH coverage is calculated using Equation 7.3

\[
\text{Coverage} = \frac{Q_1 \text{ (charge in area 1)}}{\text{charge in HAD region}} = \frac{\text{Area 1}}{\text{HAD}}
\]  

[7.3]
where

\[
\text{Area 1} = \frac{Q_1 (\mu C/cm^2)(0.1 m^2_{Pt}/cm^2)}{210 (\mu C/cm^2_{Pt})[Pt loading(mg/cm^2)]}
\]  \hspace{1cm} [7.4]

Figure 7.6 defines the HAD and Pt oxide region (Area 1). All the PtOH coverage values were calculated following this method. The dash-dotted line represents the baseline for charge integration.

![Figure 7.6: Illustration of Pt oxide coverage calculation. Dash-dotted line represents the charge integration baseline.](image)

### 7.3.3.1 Time Dependence of Pt Oxide Coverage

**Experimental data** - During the cathode potential hold in N₂, the Pt oxide changes with time. In this section, the time dependence of the Pt oxide coverage was studied. The potential holding time was varied from 5 sec to 120 min at 0.8, 0.85 and 0.9 V RHE.
Figure 7.7 shows the CVs with potential hold at 0.85 $V_{\text{RHE}}$, showing that longer holding time results in higher oxide coverage, reaching equilibrium in approximately 45 minutes, as indicated in Figure 7.8, which shows the PtOH coverage changes with time at 0.8, 0.85 and 0.9$V_{\text{RHE}}$; at each holding potential the coverage is normalized by the maximum coverage obtained at 120 min. At all holding potentials, the Pt oxide coverage reaches a plateau at ~45min even though the oxide reduction peak shifts to more negative potential with time. However, the charge passed to reduce the Pt oxide does not change in the time span of 45 min to 2hr.

---

**Figure 7.7**: Cyclic voltammograms with various potential holding time at 0.85$V_{\text{RHE}}$, 80°C and 100%RH with N$_2$ feed on the cathode.
Figure 7.8: PtOH coverage normalized to the maximum coverage within 2 hr as a function of time and potential at 80°C and 100%RH. $p_T$ = 150 kPa$_{abs}$. Data points at 0.85 and 0.9V$_{RHE}$ were the average of two independent measurements, and the error bars represent the maximum and minimum deviation from the average, respectively. There’s only one set of data at 0.8V$_{RHE}$.

**Kinetic Model for Pt Oxide Formation** – As shown in Equation 7.1, the Pt is assumed to react with H$_2$O to form PtOH, H$^+$ and e$^-$. To predict the temporal dynamics of PtOH formation upon changing potential, a kinetic model is proposed. The dependence of PtOH coverage ($\theta$) on time is described as

$$\frac{d\theta}{dt} = k_1 a_{H_2O} (1 - \theta) e^{\alpha FE / RT} - k_2 a_{H^+} \theta e^{-\beta FE / RT}$$

[7.5]
where \( k_1 \) is the forward reaction rate constant, \( a_{H_2O} \) is water vapor activity, which is equivalent to RH (in fraction), \( \theta \) is the PtOH coverage, \( k_2 \) is the backward reaction rate constant, \( a_{H^+} \) is the proton activity in the electrolyte. \( E \) is the potential across the interface; here it refers to the H\(_2\)-fed anode electrode. It should be noted that equation 7.5 assumes that one monolayer of OH (\( \theta = 1 \)) is the limiting case (e.g., 1-\( \theta \) term goes to zero).

Equation 7.5 can be rewritten as

\[
\int_0^\theta \frac{d\theta}{1 - \left[ 1 + \frac{k_2 a_{H^+}}{k_1 a_{H_2O}} e^{-(\alpha+\beta)FE/RT} \right] \theta} = k_1 a_{H_2O} e^{\alpha FE/RT} \int_0^t dt \quad [7.6a]
\]

and integrated to give

\[
\ln(1 - A \theta) = -Bt \quad [7.6b]
\]

where

\[
A = 1 + \frac{k_2 a_{H^+}}{k_1 a_{H_2O}} e^{-(\alpha+\beta)FE/RT} \quad [7.7]
\]

and

\[
B = A k_1 a_{H_2O} e^{\alpha FE/RT} \quad [7.8]
\]

therefore

\[
\theta = \frac{1}{A} (1 - e^{-Bt}) \quad [7.9]
\]
When $t \to \infty$

$$\theta_\infty = \frac{1}{A} = \frac{1}{1 + \frac{k_2 a_{H^+}}{k_1 a_{H_2O}} e^{-(\alpha + \beta)FE/RT}}$$  \[7.10\]

where $\theta_\infty$ is the PtOH coverage corresponding to $t_\infty$. Here, $\theta_\infty$ is considered as the equilibrium coverage at $t \geq 45\text{min}$ as has been established experimentally. Combining Equations 7.7-7.10, one gets

$$\frac{\theta}{\theta_\infty} = 1 - e^{-\left(k_1 a_{H_2O} e^{\alpha FE/RT} + k_2 a_{H^+} e^{-\beta FE/RT}\right) t}$$  \[7.11\]

The ratio of $\theta / \theta_\infty$ corresponds to the normalized PtOH coverage $\theta_{\text{norm}}$ shown in Figure 7.8. If it is represented by $\theta_{\text{norm}}$, rearranging Equation 7.11 and taking logarithm on each side gives

$$\ln(1 - \theta_{\text{norm}}) = (k_1 a_{H_2O} e^{\alpha FE/RT} + k_2 a_{H^+} e^{-\beta FE/RT}) t$$  \[7.12\]

For a potential of $E \gg 0$, the second exponent is negligible, and consequently Equation 7.12 becomes

$$\ln(1 - \theta_{\text{norm}}) = -(k_1 a_{H_2O} e^{\alpha FE/RT}) t$$  \[7.13\]

Figure 7.9a shows the plot of $\ln(1-\theta_{\text{norm}})$ as a function of time. The data points for a very short time ($t<1\text{min}$) and at equilibrium are not included. The absolute value of the slope is $k_1 a_{H_2O} e^{\alpha FE/RT}$. If we take natural logarithm of each slope and plot them versus potential, as shown in Figure 7.9b, a new slope is obtained representing the $\alpha F/RT$. Thus $\alpha$ is
determined as 0.14, which implies that the overpotential is heavily biased toward the reduction of the oxide. The intercept is \( \ln(k_1a_{H_2O}) \).

Figure 7.9: (a) Normalized PtOH coverage as a function of time at various potentials and (b) Derivation of \( \alpha \) for PtOH formation at 80°C and 100%RH.
Darling and Meyers\textsuperscript{12} reported equilibrium potential for the reactions (from Pourbaix diagram)

\[\text{Pt} + \text{H}_2\text{O} \leftrightarrow \text{PtO} + 2\text{H}^+ + 2\text{e}^- \quad E^\circ_1 = 0.98\text{V} \quad [7.14a]\]

and

\[\text{Pt} \leftrightarrow \text{Pt}^{2+} + 2\text{e}^- \quad E^\circ_2 = 1.188\text{V} \quad [7.14b]\]

\[\text{PtO} + 2\text{H}^+ \leftrightarrow \text{Pt}^{2+} + \text{H}_2\text{O} \quad k = 3.2 \times 10^{-24} \text{ mol/cm}^2\text{s} \quad [7.14c]\]

It is expected that the standard potential for reaction 7.1 is smaller than 0.98V, as it is assumed that this reaction occurs earlier than reaction as shown by 7.14a. The agreement between the experimental data and the proposed kinetic mechanism for PtOH formation hints that PtOH is probably the first product to form on the Pt surface.

### 7.3.3.2 Effects of $\text{O}_2$ Exposure on Pt Oxide Coverage

Figure 7.10 shows the CVs and integration baseline obtained in a H\textsubscript{2}/N\textsubscript{2} cell with initial holding potentials ranging from 0.6 to 0.9 $V_{\text{RHE}}$ at 80°C, 150kPa\textsubscript{abs}, and 100%RH. The charge required to reduce the Pt oxide strongly depends on the potential, decreasing from maximum at 0.9 $V_{\text{RHE}}$ down to very little at 0.6 $V_{\text{RHE}}$. The charge passed to reduce the Pt oxide was integrated relative to the integration baseline over the potential range from the initial holding potential down to 0.35$V_{\text{RHE}}$. 
Figure 7.10: CVs obtained in a cell with 10%H₂ in N₂ on anode and N₂ on cathode at 80°C, 150 kPa abs, and 100%RH with different initial hold potential for 45min (0.6 to 0.9V vs. RHE). The dash-dotted line represents the charge integration baseline.

Figure 7.11 shows the CVs collected after holding at a potential of 0.85 V RHE for the various exposure cases, along with the integration baseline. Unlike earlier studies, no impact of the O₂ prior exposure is observed. Figure 7.12 shows actual time traces for the 100% O₂ exposure experiment at 0.85 V RHE: 1) initial potential hold in N₂ for 5 min., 2) exposure to O₂ for 30 min., producing a current of 0.13-0.2 A/cm², 3) return to N₂, hold for 10 minutes, and 4) collection of CVs to reduce the oxide (not shown in this plot). During the O₂ exposure, the electrode voltage was controlled to as low as 0.827 V_RHE to compensate for the 0.023 V IR-drop. Had this not been done, the electrode potential
during the O₂ exposure would have been driven higher than 0.85 V<sub>RHE</sub> by about 23 mV.

The maximum IR-correction in this experimental set, for 0.65V<sub>RHE</sub> and pure O₂, was over 0.250 V.

**Figure 7.11:** CVs with initial potential hold at HFR-corrected potential of 0.85V<sub>RHE</sub> after exposure to N₂, Air, 50%O₂, and O₂ for 30min, respectively at 80°C, 100%RH, 150kPa<sub>abs</sub>. The dash-dotted line represents the charge integration baseline.
Figure 7.12: Current density, HFR, cell potential and HFR-corrected voltage as a function of time at initial applied potential of $0.85\, V_{\text{RHE}}$ with exposure to $N_2$ for 5min, then 30min exposure to $100\%\, O_2$ followed by 10min $N_2$ purging at 80°C, 100%RH, and 150kPa$_{\text{abs}}$. Dashed curves represent potential, and solid curves represent current density and HFR, respectively.

To further investigate the oxide reversibility, potential hold experiments without IR correction were also conducted with the $100\%\, O_2$ exposure at 0.6 and $0.85\, V_{\text{RHE}}$. The same results were obtained as the $N_2$ exposure even in these cases, indicating that any formation of oxide due to the exposure of the electrode to the higher IR-free potential was reversibly removed within 10 min. when the electrode was returned to the $N_2$ environment.

Figure 7.13 shows the PtOH coverages as function of potential ranging from 0.6 to $0.9\, V_{\text{RHE}}$, with exposure to $O_2$ at various concentrations. The results indicate that exposure
to O₂ had no contribution to the Pt surface oxide coverage after subsequent 10 min N₂ exposure. Figure 7.13 indicates that the PtOH coverage actually exceeds 1 at >0.85 Vₑ. In fact, some PtO is likely to form in this potential region, requiring two electrons per Pt site, such that the surface coverage remains less than unity. PtOH ↔ PtO + H⁺ + e⁻, which together with Equation 7.1 gives an overall reaction shown as Equation 7.14a. At potentials > 1Vₑ, it is well known that place exchange can occur and the Pt oxide coverage can thus exceed one.²⁵

![Figure 7.13: Comparison of measured PtOH coverage as a function of potential at 80°C, 150 kPaₐ, and 100%RH, for various prior gas exposures. The anode gas was 10%H₂ in N₂.](image-url)
The dependence of the oxide coverage on potential and not on previous O$_2$ exposure indicates that either the oxide formed by the gaseous O$_2$ is highly reversible or O$_2$ does not participate in the oxide formation reaction at all, in contrast to earlier results$^{16,17}$ The difference in set-up that most likely explains this disagreement is the use of a single manifold and humidifier system in previous studies that may have led to residual O$_2$ present in the N$_2$ stream even for the 2.5 hours after the switch over to N$_2$. Our group’s previous work also used a set-up with one single humidifier$^{19}$ and we observed, using open circuit voltage as a marker, that as much as 4 hours was required to eliminate the residual O$_2$. The temperature differences may also be a factor; the oxide reduction kinetics may be quite slow at 25°C$^{16}$ and the oxide formed at 100°C may have been more robust than that formed at 80°C.$^{17}$ The use of IR-free potential control is thought not to be responsible for the variation in results; it has been showed in this work that this factor made little difference, as long as the electrode was returned to N$_2$ for at least 10 minutes to allow the system to return to equilibrium.

The Pt oxide coverages shown in Figure 7.13 are regarded as the equilibrium coverages at various potentials. Equation 7.10 can be rewritten as

\[
\frac{1}{\theta_x} - 1 = \frac{k_2a_{H^+}}{k_1a_{H_2O}} e^{-\left((\alpha + \beta)FE / RT\right)}
\]  

[7.15a]

Taking natural logarithm on both sides gives

\[
\ln\left(\frac{1}{\theta_x} - 1\right) = \ln\left(\frac{k_2a_{H^+}}{k_1a_{H_2O}}\right) - \left((\alpha + \beta)FE / RT\right)
\]  

[7.15b]
Using the averaged Pt oxide coverage at each potential in Figure 7.13, the correlation between the \( \ln(1/\theta_{\infty} - 1) \) and potential is as shown in Figure 7.14 in excellent agreement with the model (Equation 7.15b). Data point greater than 1 is not included in the plot because further oxidation to PtO probably occurs at the potentials greater than 0.85V. The slope is \(- (\alpha + \beta)F/RT = -31.04\), thus \(\alpha + \beta = 0.94\) and \(\beta = 0.8\). This is very encouraging because one would expect that \(\alpha + \beta = 1\). The obtained results imply that the model for PtOH formation described in previous section is in good standing. The intercept in Figure 7.14 represents \(\ln\left(\frac{k_2 a_{H^+}}{k_1 a_{H_{2}O}}\right)\).

![Graph](image)

**Figure 7.14**: Experimental data for Equation 7.15b.

### 7.3.3.3 RH Effect on Pt Oxide Coverage

The effect of RH on the formation of Pt oxide is shown in Figure 7.15, which
indicates that at the same potential, the coverage increases with increasing RH, especially at potentials of 0.75V_{RHE} or above. This is consistent with the fact that H_2O is a reactant in the Pt oxidation reaction (Pt + H_2O \rightarrow PtOH + H^+ + e^-), and the increase in water concentration shifts the equilibrium to the right. When the potential is at 0.65V_{RHE} or below, the PtOH coverage is low and nearly independent of the RH; even at fully humidified condition the coverage is only about 0.14. Each data point is obtained by averaging results from at least three independent measurements. The error bars represent the maximum and minimum deviation from the averaged value.

![Graph](image)

**Figure 7.15:** PtOH coverage at 80°C, 100%, 75%, 50% and 35%RH. Each point is the average value of at least three samples. The error bars represent the maximum and minimum deviation from the average value, respectively.
Having the PtOH coverage as a function of potential at various RH, it is of interest to know how the equilibrium coverage at each potential changes with RH. Equation 7.15a is rearranged to become

\[
\frac{1}{\theta_\infty} = 1 + \frac{k_2a_{H^+}}{k_1a_{H_2O}} e^{-(\alpha+\beta)FE/RT} \tag{7.16}
\]

The data shown in Figure 7.15 is plotted, according to the above equation, in Figure 7.16a showing the $1/\theta_\infty$ versus the reciprocal of the water RH (or $a_{H_2O}$). Here, the $a_{H^+}$ and the standard potential $E^o$ are assumed to be independent of RH. Figure 7.16a shows that at each potential, $1/\theta_\infty$ is linearly proportional to the reciprocal of RH. At each potential the slope is $\frac{k_2a_{H^+}}{k_1} e^{-(\alpha+\beta)FE/RT}$, thus increasing potential should decrease the slope. This trend is followed very clearly in Figure 7.16b, increasing the confidence in the kinetic model. Taking logarithm of the slopes and plotting them versus potential, as shown in Figure 7.16b, the new slope is $-(\alpha+\beta)F/RT=-11.78$, leading to $(\alpha+\beta)=0.36$, in disagreement with $(\alpha+\beta)=0.94$ as previously obtained from Figure 7.14. Clearly the assumption that $a_{H^+}$ is independent of RH is incorrect. $a_{H^+}$ depends on RH due to swelling. The linearity and the slope of Figure 7.16b can be substantially improved once these effects are considered. If the data at 0.9V is omitted, the slope becomes -16.77 resulting in $(\alpha+\beta)=0.51$, much closer to 0.94. Further effort is needed to obtain the reaction rate constants and stand potential for the PtOH formation.
Figure 7.16: (a) Correlation between $1/\theta_\infty$ and $1/RH\%$ at various potentials and (b) logarithm of the slopes as shown in Figure 7.16a versus potential at 80°C in H$_2$/N$_2$. 
7.3.3.4 Temperature Effect on Pt Oxide Coverage

As shown in Figure 7.3, the HAD areas are nearly independent of temperature (30 to 90°C) though the characteristic peaks shifted slightly in a more negative direction with increasing temperature. The effect of temperature on Pt oxide formation was also measured in the high potential region. Figure 7.17 shows a series of CVs at various temperatures while holding the potential at 0.85V. In the high potential region, the area representing the charge passed to reduce the Pt oxide species, increases with increasing temperature, while the HAD is nearly independent of temperature (30 to 90°C). These observations could be attributed to the slow kinetics of Pt oxide formation and to the fast kinetics of H-adsorption/desorption in the temperature range studied. The PtOH coverage as a function of temperature at various holding potentials is shown in Figure 7.18. At each holding potential, the PtOH coverage increases with increasing temperature.
Figure 7.17: Cyclic voltammograms at various temperatures (30°C to 90°C) with potential hold at 0.85V_RHE for 45min in a H₂/N₂ (flow rate 200/50 sccm) cell at 100%RH. At each potential, the holding time was 45min before collecting the CVs.
7.4 SUMMARY

Hydrogen crossover current has strong dependence on cell potential: at potential < 0.2V, the HOR is kinetically controlled so that the current increases with increasing potential; in the potential range of 0.2-0.75V, HOR current is permeation-limited, is independent of potential; at potential of about 0.75V or above, the HOR current decreases with increasing potential, indicating that HOR kinetics is affected by the Pt oxide coverage on the catalyst. Using diluted H₂ on the anode could greatly reduce the background signal error. The dependence of HOR on the Pt oxide coverage suggests that the ORR conducted at high cathode potentials need to consider the effect of reduced
H₂ crossover current. The fact that HOR becomes slower at higher cathode potentials explains the observed H₂ slip at the cathode exit when H₂ is supplied into the cathode to assist fuel cell cold start.

The HAD areas are found to be independent of cell temperature (30°C to 90°C at 100%RH) and RH (35%-100% at 80°C). Each of the characteristic peaks’ positions moves to more negative potentials with increasing temperature or decreasing RH. The equilibrium surface coverage of cathode Pt oxide in PEM fuel cells was investigated by quantifying the charge passed to reduce the oxide using cyclic voltammetry. Charges passed to reduce the Pt oxide formed on Pt/Vulcan catalyst increases with increasing potential, temperature or RH. It takes about 45min for the Pt oxide coverage to reach steady state at a holding potential. A model was introduced to study the kinetics of PtOH formation. The obtained charge transfer coefficient (α=0.14, β=0.8) indicates that the PtOH formation is more sluggish than its reduction. Excellent agreement between the experimental data and the model is observed. Further analysis shows that the standard potential for PtOH formation most likely depends on the water activity or RH. The general agreement between the experimental data and the proposed kinetic model for the reaction between Pt and water to form PtOH indicates that PtOH is probably the first product to cover the Pt surface.

A separated humidifier for N₂ purging on the cathode can effectively deplete the residual O₂ in the cell. The coverage of Pt oxide does not depend on previous exposure to O₂, indicating that the Pt oxidation by gaseous O₂ is reversible. The study demonstrates the importance of understanding the role of Pt oxide in the ORR kinetics, and it provides a methodology useful for screening new ORR catalysts.
In summary, Pt oxide coverage has been measured as a function of potential, history of prior exposure to O₂, RH and temperature. At 80°C and 100% relative humidity, in the range of HFR-corrected potential from 0.6 to 0.9V_{RHE}, the measured coverage of Pt oxide is a function of the potential, but not a function of the partial pressure of O₂, under the same amount of the potential holding time. The results and the kinetic model can be used to improve HOR and ORR kinetics and to accurately predict the of HOR current in the O₂ environment, as well as to predict the ORR kinetic loss contributions at various cathode potentials.

**SYMBOLS**

\( a_{H_2O} \)     water vapor activity  
\( a_{H^+} \)     proton concentration in electrode mol/cm³  
\( E \)           potential, V  
\( E^0 \)         standard potential for PtOH formation by H₂O, V  
\( F \)           Faraday’s constant, C/eq  
\( k_1 \)         PtOH formation reaction rate constant  
\( k_2 \)         PtOH reduction reaction rate constant  
\( R \)           universal gas constant, J/(mol·K)  
\( t \)           time, min  
\( T \)           temperature, °C or K  

**Greek**

\( \alpha \)       transfer coefficient  
\( \beta \)        1-\( \alpha \)  
\( \theta \)       Pt oxide coverage  
\( \theta_e \)      Pt oxide coverage at equilibrium
REFERENCES


Chapter 8

Summary and Future Work Recommendations

8.1 SUMMARY

This thesis studies proton conduction in proton exchange membrane (PEM) fuel cell cathodes. A method using AC impedance was established to measure this resistance using a H₂/N₂ cell, which was designed to operate under differential conditions. This setup guarantees the reliability of the measurements, excluding any uncertainties resulting from RH variations across the cell. The impedance data were analyzed by a 1-D transmission-line model, assuming uniform ionomer and capacitance throughout the entire cathode thickness. The assumptions are tested by measuring proton resistance of cathodes with various thicknesses. The effects of various cathode properties, such as ionomer content, ionomer conductivity, and Pt-dispersed carbon supports, were investigated using the AC impedance technique. A thin shell model was introduced to establish a correlation between the electrode composition and the electrode proton resistivity normalized by the ionomer resistivity. The normalized electrode proton resistivity was found to intrinsically depend on the volumetric \((I/C)_{v}\) ratio. Cell voltages were acquired for electrodes with various cathode compositions under various conditions. A 1-D water transport model was developed and evaluated to determine the water profile across the cell as a function of current density and inlet RHs. The measured cathode proton resistance and predicted water profile were incorporated, and applied to the 1-D H₂/O₂ cell performance model. The observation was further discussed by comparing data
with model predictions. The Pt surface coverage and the kinetics of PtOH and PtO formation were investigated and modeled in terms of the residence time, temperature, potential, and operating conditions.

With all the above mentioned studies, some important results and findings are summarized by the following:

• A well-defined experimental method using AC impedance in H2/N2 for measuring the cathode proton resistance is developed. The obtained impedance spectra can be effectively analyzed by a 1-D transmission-line model. The analysis of the through-plane membrane resistivity indicates the necessity to consider its swelling behavior, especially above 75%RH.

• The cell voltage losses caused by proton conduction in the cathode strongly depend on the ionomer-carbon (I/C) weight ratio and relative humidity (RH). Given the same RH the cell voltage decreases with decreasing I/C and decreases with decreasing RH at the same I/C.

• The Pt electrochemical area is independent of the studied range of I/C-ratio for Pt/V electrode (0.3-1.2) and RH (35%-122%) as well as the Pt-specific capacitance.

• One merging curve of tortuosity in the electrode for the proton conduction is obtained if the ionomer swelling behavior is taken into account. The tortuosity is nearly 1 when there is enough ionomer (I/C>0.6), however, for I/C<0.6, the tortuosity increases dramatically with decreasing I/C. This point is regarded as a percolation threshold, a critical I/C at which the ionomer network interrupted.
• The proton resistance obtained in H₂/N₂, is validated by applying it to a H₂/O₂ cell at low current density under differential conditions.

• The resistance-corrected cell voltage is nearly independent of the RH and I/C. By comparing the data and theoretical values, it is concluded that the RH has a minor effect on the oxygen reduction reaction (ORR) kinetic, within 30mV at 35% cathode RH.

• The proton resistivity is independent of the electrode thickness for uniformly prepared electrodes. This validates the assumptions in the transmission-line model that the ionomer and capacitance are uniformly distributed throughout the entire electrode thickness.

• Changing the ionomer EW directly affects the electrode proton resistivity. The density of SO₃H group in the electrode determines the proton resistivity. Above certain SO₃H density (>0.35 mmol/cm³ electrode), the difference in proton resistivity of electrodes with different EW ionomers is undetectable.

• When the ionomer film on the carbon is ultra thin, the mechanism of proton conduction through this layer might be different from the one in the bulk membrane. It is possible that in such an ultra thin ionomer layer the role of a thin aqueous layer formed on the face of the ionomer dominates the bulk Gierke mechanism. It is possible that the SO₃H groups undergo transformation, pointing toward the face of the ionomer, collecting water there.

• The cell performance is affected by the ionomer EW: cathodes with lower EW ionomer exhibit higher cell voltage than cathodes with higher EW ionomer at low
I/C-ratios and low RH levels due to increased -SO\textsubscript{3}H density. However, at a fully humidified condition, low EW cathodes poorly perform probably because of the higher water uptake capability, which can cause flooding. Given the same Pt loading the HFR and electrode’s proton resistance-corrected voltage are independent of I/C-ratio at all RH levels regardless of the ionomer conductivity.

- The correlation between electrode proton resistivity and ionomer resistivity is described by a simple thin-shell model assuming the carbon particles to be spheres. It is demonstrated that the normalized proton resistivity depends intrinsically on the volumetric ratio of I/C taking the ionomer swelling behavior into account.

- The comparison between the thin shell model and experimental data indicates that some portion of ionomer does not contribute to the proton conduction in the electrode. The difference between the added \((I/C)_v\) and the effective one indicates that \(~0.3-(I/C)_v\) amount of ionomer is absorbed into the Vulcan pores, or becomes ineffective inside the roughness crevices, and \(~0.46-(I/C)_v\) amount of ionomer is absorbed into the KB pores. The roughness factor is \(~1.6\) for Pt/V catalyst, and \(~4\) for Pt/KB catalyst.

- The effect of various carbon supports on cathode proton resistivity is compared between cathodes with Pt/V and Pt/KB catalysts, given the same ionomer is used. The Pt/KB cathodes show much higher proton resistivity and tortuosity than the Pt/V cathodes because of its higher carbon surface roughness and porosity given the same I/C ratio. It is estimated that a significant fraction of the ionomer absorbed inside the KB carbon resulting in higher resistivity.
• The higher adsorption of ionomer into the inner pores and the catalyst surface roughness account for the larger proton resistivity of Pt/KB cathode than of the Pt/V cathode, by a factor of 3-4.

• At RH ≥ 50% the cell performance of Pt/KB cathode is superior to that of the Pt/V cathode due to its higher Pt surface area. However, at drier conditions the performance of Pt/V cathode is better because its lower proton resistivity dominates.

• A comparison of the calculated iR-corrected cell voltage with the measured values for Pt/V and Pt/KB cathode further indicates that the ORR kinetics does not have a strong dependence on RH.

• A 1-D model based on water transport in a complete H₂/O₂ cell is presented describing the local RH distribution in the membrane and the electrodes under various conditions. The predicted RH distribution was validated by two methods: Comparison to the experimental membrane resistance; Comparison of the experimentally measured cell voltage to that predicted by the cell performance model. Both comparisons gave good agreement although the model overpredicts the cell voltage at low RH and high current density. The discrepancy in local RH obtained from the two approaches implies the possible existence of additional voltage losses unaccounted for by the model. Possible reasons causing this discrepancy are investigated by assuming a certain level of errors in transport parameters.

• The validated water transport model allows the prediction of undesirable dryout, liquid water formation in the electrodes and possible flooding. Furthermore, it allows one to predict the water fluxes toward the anode and the cathode and their dependence on operating conditions. The flux of water from the cathode through the
DM into the cathode’s FF is assumed to be either gaseous or liquid, and its effect on the counter diffusion of oxygen in the cathode is evaluated. Gaseous water presents negligible flow to overcome, yet a flow of liquid water can present flooding if water is inefficiently removed from the DM into the FF.

- Hydrogen crossover current has strong dependence on cell potential: at potential $<0.2\text{V}$, the HOR is kinetically controlled so that the current increases with increasing potential; at potential of about $0.75\text{V}$ or above, the HOR current decreases with increasing potential, indicating that HOR kinetics is affected by the formation and coverage of Pt oxide on the catalyst.

- H-adsorption/desorption are independent of cell temperature (30°C to 90°C at 100%RH) and RH (35%-100% at 80°C). Each of the characteristic peaks’ positions moves to more negative potentials with increasing temperature or decreasing RH.

- Equilibrium surface coverage of cathode Pt oxide in PEM fuel cells was investigated by quantifying the charge passed to reduce the oxide using cyclic voltammetry. The Pt oxide coverage increases with increasing potential, temperature or RH. It takes about 45min for the Pt oxide coverage to reach steady state at the holding potential.

- A model was introduced to study the kinetics and dynamics of PtOH formation. The obtained charge transfer coefficient ($\alpha=0.14$) indicates that the PtOH formation is more difficult than its reduction. Further analysis shows that the standard potential for PtOH formation is possibly dependent on water activity.

- Residual O$_2$ in the cell can be effectively removed by using a separated humidifier for N$_2$ pumping in the cathode FFs. The amount of Pt oxide did not depend on previous
exposure to O₂, indicating the reversibility of any oxidized species generated in the presence of gas-phase O₂. The study demonstrates the importance of understanding the role of Pt oxide on the ORR kinetics, and it provides a methodology for effective screening of new ORR catalysts.

8.2 FUTURE WORK RECOMMENDATIONS

**Nonuniform Cathodes**

Much effort has been invested toward the determination of cathode proton resistance and its applications. However, the analysis tool for the impedance spectra is limited to uniformly distributed porous electrodes. Of value would be the development of a comprehensive model for various types of electrodes: catalyst coated diffusion media (CCDM) electrode, where difficulty in controlling ionomer content in the electrode is experienced due to ionomer leach into the diffusion media during the assembly; NSTF electrode, where there is no ionomer in the electrode and a model considering the role of water might be necessary; electrodes with non-carbon support material, such as a semiconductor (e.g., TiO₂), which itself has a strong impedance signal upon changing potential, current, or treatment history. It will be of great interest to develop a model capable of addressing these concerns.

**Mechanism of Proton Conduction in Ultra Thin Ionomer Layers**

As illustrated in Chapter 3, the mechanism of proton conduction through an ultra thin ionomer layer (<1nm) in the electrode remains an open question. The possible formation of an aqueous layer on the face of the thin layer has been suggested. The mechanism of proton conduction in this thin aqueous layer is obviously different from the bulk
mechanism due to the ionomer structure change. The observed difference in proton resistivity of electrodes with different EW ionomers has triggered a second thought on the configuration of an ultra ionomer in the electrode. The question remains whether or not it requires phase transformation from bulk to surface sulfonic acid groups.

In Chapter 4, the thin shell model for proton conduction in the electrode assumes the carbon particles as spheres and cubically packed. The comparison between the model and the experimental data illustrates the necessity to consider the carbon roughness and porosity, both adversely contributing to the absorption of ionomer. The seeming conflict between the two mechanisms should be resolved. The effect of carbon packing pattern was not discussed in this work so it is unclear whether or not this is an important aspect.

**Water Management**

The RH distribution was investigated in Chapter 6. The discrepancy between the measured and predicted cell voltage hints that there might be unknown voltage losses unaccounted for, such as additional ORR overpotential resulting from the RH, oxygen transport or Pt oxide coverage effects.

**Pt Oxide Coverage**

In Chapter 7, the Pt oxide coverage was investigated only in an O\textsubscript{2}-free environment, where the oxide formation is due to Pt reaction with water. In order to incorporate these two oxidation reactions into the ORR kinetics, the kinetics of the formation of Pt oxide under an O\textsubscript{2} environment is highly desirable. Modeling the kinetics of PtOH formation was initiated in Chapter 7, and some very encouraging kinetics results have been obtained. Further investigation into Pt oxide formation under ORR kinetics is highly recommended.
APPENDICES
Appendix A: Ionomer Volume Fraction in Electrode

The ionomer volume fraction ($\varepsilon_i$) of the cathode at any RH is defined

$$\varepsilon_i \equiv \frac{V_{I,wet}}{V_{cath}} = \left(\frac{I}{C}\right) \cdot \left(\frac{10^{-3} \cdot m_c \cdot A}{m_{I,dry}}\right) \cdot \left(\frac{V_{I,wet}}{V_{cath}}\right)$$  \[A.1\]

where $V_{I,wet}$ is the volume of ionomer as a function of RH, $I/C$ is the weight ratio of ionomer to carbon in the electrode, $m_c$ is the Carbon loading in the electrode in the unit of mgC/cm$^2$, $A$ is the active area of the MEA, which is 50cm$^2$ in this study, and $m_{I,dry}$ is the mass of dry ionomer in grams. The subscripts “wet” and “dry” refer to ionomer that is at least partially humidified or completely dry, respectively. $V_{cath}$ is the volume of cathode catalyst layer, which is defined as

$$V_{cath} = 10^{-4} \cdot A \cdot t_{cath} = 10^{-4} \cdot A \cdot (f_t \cdot m_c)$$  \[A.2\]

where $10^{-4}$ is a unit conversion factor in order for $V_{cath}$ to have a unit of cm$^3$, $t_{cath}$ is the cathode thickness, and $f_t$ is 28 ± 2µm/(mgC/cm$^2$) for I/C of <3/1. The ionomer volume is given by the following equation based on Equation 3.4 in the text,

$$V_{I,wet} = V_{I,dry} \cdot \left(1 + \frac{M_w \cdot d_{I,dry} \cdot \lambda}{d_w \cdot EW}\right) = \frac{m_{I,dry}}{d_{I,dry}} \cdot \left(1 + \frac{M_w \cdot d_{I,dry} \cdot \lambda}{d_w \cdot EW}\right)$$  \[A.3\]

where $d_{I,dry}$ is the density of dry ionomer equivalent to $d_{mem,dry}$ as defined previously in the text, which is≈2g/ cm$^3$, $d_w$ is the density of water (equal to 0.97g/cm$^3$ at 80°C), the values of $\lambda$ is calculated from Equation 2.2, and EW is the equivalent weight of the
ionomer in the electrode, which is 1050 g/mol\textsubscript{H⁺}. Dividing Equation A.3 by Equation A.2
leads to

\[ \frac{V_{I,\text{wet}}}{V_{\text{cath}}} = \left( \frac{m_{I,\text{dry}}}{10^{-3} \cdot m_c \cdot A} \right) \cdot \left( \frac{10}{f_t \cdot d_{I,\text{dry}}} \right) \cdot \left( 1 + \frac{M_w \cdot d_{I,\text{dry}} \cdot \lambda}{d_w \cdot EW} \right) \]  

[A.4]

Finally, insert Equation A.4 to A.1 to give:

\[ \varepsilon_i = \left( \frac{I}{C} \right) \cdot \frac{10}{f_t \cdot d_{I,\text{dry}}} \cdot \left( 1 + \frac{M_w \cdot d_{I,\text{dry}} \cdot \lambda}{d_w \cdot EW} \right) \]  

[A.5]
Appendix B: Dry Ionomer Density

The recast membrane from the ionomer solution absorbs water when it is exposed to air. Its weight \( m_{\text{mem,wet}} \) includes the mass of the dry membrane \( m_{\text{mem,dry}} \) and the absorbed water \( m_w \) as shown in Equation B.1:

\[
m_{\text{mem,dry}} + m_w = m_{\text{mem,wet}}
\]  \[\text{[B.1]}\]

The mass of water can also be determined from the amount of \( -\text{SO}_3\text{H} \) group contained in the membrane at a certain temperature and RH as shown in Equation B.2:

\[
m_w = m_{\text{mem,wet}} - m_{\text{mem,dry}} \equiv M_w \lambda m_{\text{mem,dry}}/EW
\]  \[\text{[B.2]}\]

where \( M_w \) is the molecular weight of water in unit of g/mol, \( \lambda \) is the number of water molecules per \( -\text{SO}_3\text{H} \) group. Equations B.1 and B.2 are combined to give:

\[
m_{\text{mem,dry}} = m_{\text{mem,wet}} \left( \frac{\lambda M_w}{1 + \frac{\lambda M_w}{EW}} \right)
\]  \[\text{[B.3]}\]

The total volume \( V_{\text{mem,wet}} \) of the recast membrane is the sum of the volumes of dry membrane and absorbed water as shown in Equation B.4:

\[
\frac{m_{\text{mem,dry}}}{d_{\text{mem,dry}}} + \left( \frac{m_{\text{mem,wet}} - m_{\text{mem,dry}}}{d_w} \right) = V_{\text{mem,wet}}
\]  \[\text{[B.4]}\]

where \( d_{\text{mem,dry}} \) (g/cm\(^3\)) is the density of the dry membrane, \( d_w \) (g/cm\(^3\)) is the density of water. Insert Equation B.3 into Equation B.4, and rearrange the equation to give:
\[ d_{\text{mem,dry}} = \frac{E W \cdot d_{\text{mem,wet}}}{(E W + \lambda M_w) - \frac{M_w \lambda d_{\text{mem,wet}}}{d_w}} \]  

[B.5]

d_{\text{mem,wet}} is the density of the wet membrane at certain temperature and RH, which could be obtained by dividing mass of the wet membrane \( m_{\text{mem,wet}} \) by its volume \( V_{\text{mem,wet}} \).
Appendix C: Sketches of a PEM Fuel Cell with 5cm² Active Areas on Cathode

A: Flow field and current collector
B: Alignment pin hole
C: Flow channel
D: Gasket
E: Diffusion media
F: Catalyst layer
G: Membrane
Appendix D: Reynolds Numbers for Gas mixture in Anode and Cathode FFs

The gas flow rate on each side is 3500sccm. The cross section of the 6-channel flow field, 
A= 6 × (0.84 × 0.3) = 1.512mm², so the velocity of the gas flow 

\[ v = \frac{3500 \text{sccm}}{(1.512 \times 10^{-2} \text{cm}^2)} = 231481 \text{cm/min} = 38.6 \text{m/s} \]

Reynolds number is described as

\[ \text{Re} = \frac{d v}{\nu} \quad [\text{D.1}] \]

where \( d \) (0.03cm), the characteristic length, is the FF channel depth, \( v \) is the velocity (38.62m/s), and \( \nu \), the kinematic viscosity, is ratio of its dynamic viscosity (\( \mu \)) to density (\( \rho \)). At 80°C and 100%RH, the \( \mu \) and \( \nu \) of H₂, O₂, H₂O and their mixture are listed in Table D.1. The values are referenced from Perry’s Chemical Engineers’ Handbook (1973).

**Table D.1**: Viscosity, density, and Reynolds numbers for gas mixture in anode and cathode FFs at 80°C, and 250kPa reactant partial pressure.

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>( M ) (g/mol)</th>
<th>( \rho ) (kg/m³)</th>
<th>( \mu \times 10^6 ) (Pa·s)</th>
<th>( \nu \times 10^6 ) (m²/s)</th>
<th>( \text{Re} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (250kPa)</td>
<td>2</td>
<td>0.1726</td>
<td>10.03</td>
<td>58.11</td>
<td>n/a</td>
</tr>
<tr>
<td>O₂ (250kPa)</td>
<td>32</td>
<td>2.76</td>
<td>23.43</td>
<td>8.49</td>
<td>n/a</td>
</tr>
<tr>
<td>H₂O (47.3kPa)</td>
<td>18</td>
<td>n/a</td>
<td>11.19</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>H₂O+H₂ 75%RH</td>
<td>3.98</td>
<td>0.3439</td>
<td>11.18</td>
<td>32.51</td>
<td>409</td>
</tr>
<tr>
<td>H₂O+H₂ 25%RH</td>
<td>2.72</td>
<td>0.2346</td>
<td>10.54</td>
<td>44.93</td>
<td>272</td>
</tr>
<tr>
<td>H₂O+O₂ 75%RH</td>
<td>30.26</td>
<td>2.61</td>
<td>21.90</td>
<td>8.39</td>
<td>1588</td>
</tr>
<tr>
<td>H₂O+O₂ 25%RH</td>
<td>31.37</td>
<td>2.71</td>
<td>22.92</td>
<td>8.46</td>
<td>1443</td>
</tr>
</tbody>
</table>

Table D.1 indicates that \( \text{Re} \leq 2300 \), so it is under laminar flow under each condition in this study.