

Proton Transport and Durability of Polymer Electrolyte Membrane Fuel Cells' Catalyst Layer

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Abstract

Polymer electrolyte membrane fuel cells (PEMFCs) are promising power sources for transportation applications due to their low carbon dioxide emission, and high energy efficiency features. However, there are still some problems that hinder the wide commercialization of fuel cell electric vehicles (FCEVs), including poor durability, and high cost. For the state-of-the-art PEMFC system, the cost of catalyst still takes about 30% of the total cost. The cost of fuel cell system is still above the Department of Energy (DOE) 2020 cost target of 40 \$/KW. As platinum (Pt) is still the most commonly used catalyst for PEMFC, it is hard to reduce this portion of raw material cost by mass production. Within the fuel cell, the oxygen reduction reaction (ORR) that happens at the cathode has very sluggish kinetics compared with the hydrogen oxidation reaction (HOR) that happens at the anode. Because of that, the fuel cell cathode requires much more loading of catalyst than the anode. Though there has been a lot of progresses in the development of alternative non-platinum group metal (non-PGM) catalysts, the specific activity and durability are still not comparable with conventional Pt catalyst. In the near term, increasing the utilization of Pt is a more viable solution to reduce the catalyst loading and cost while maintaining the required power density. Scientists and engineers have put significant efforts into developing new platinum group metal (PGM) catalyst using alloying or nano-structuring techniques. Another approach that is of equivalent importance is to make the catalyst surface area electrochemically accessible, without contact with the polymer electrolyte that

poisons the catalyst. Part of this dissertation, we studied the proton transport properties of a new ionomer-free catalyst configuration, and the ionomer-free regions in the conventional carbon supported Pt catalyst (Pt/C) catalyst. The water and electrode potential dependence of the proton transport process were studied in detail. The information will be instructive to new catalyst structure design and operating condition optimization.

Another issue challenging automotive PEMFC systems is their durability. Unlike stationary power system, automotive applications requires the PEMFC system to experience quick variation of power demand, a wide variety of weather conditions, including sub-freezing conditions, and thousands of cycles of start-up/shutdown processes. The power demand variation and subfreezing condition operation can occasionally cause hydrogen starvation in the fuel cell catalyst layer, leading to cell reversal and potentially carbon corrosion damage. Start-up/shutdown cycles can also lead to electrolyte potential perturbations and slow degradation to the cathode. In this work, we examined the hydrogen starvation at regular temperatures by looking at the oxygen evolution reaction (OER) catalyst failure mechanism at the anode, and tested a new anode configuration with enhanced reversal tolerance. We also studied the degradation mechanism related to subfreezing condition operations. As for the start-up/shutdown cycle durability, we tested a series of selective anode catalysts and their effectiveness in preventing cathode degradation.

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Chapter 1

Introduction

1.1 Motivation

Polymer electrolyte membrane fuel cell (PEMFC) uses hydrogen as the fuel and generate electricity with water as the byproduct. It has been considered as a promising substitute for internal combustion engines because of its prominent advantages, including low carbon dioxide emission, high energy density, and high fuel efficiency [6]. However, for fuel cell electric vehicle (FCEV) to become commercially viable, three main challenges, i.e., performance, cost, and durability must be resolved [7]. For state of the art fuel cell systems, about 30% of the cost comes from the catalyst layer material, and the most common catalyst used is platinum (Pt) [8]. Since this high catalyst cost is a result of expensive raw material, it can not be brought down by increasing the scale of mass production. For many decades, efforts have been made to reduce the cost of the fuel cell system. Currently, the cost of fuel cell systems is still above the Department of Energy (DOE) 2020 cost target of 40 \$/KW [9]. One option is to use non-platinum group metal (non-PGM) catalyst like nitrogen activated carbon to replace Pt used in the catalyst layer [10, 11, 12]. However, this kind of catalyst's activity and durability are still lower than Pt [13]. Also, because

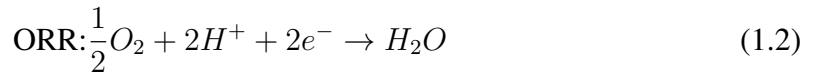
of the low specific activity of non-PGM catalyst, the catalyst layer thickness needs to be almost an order of magnitude higher than conventional carbon supported Pt catalyst (Pt/C) catalyst, leading to larger fuel cell system volume and hard to implement for vehicle applications. Many years' of development is still needed before this kind of catalyst can be comparable to conventionally used Pt catalyst. Another way to reduce the catalyst cost is to increase the specific and mass activity of Pt, so that less Pt will be needed for the same power demand, using methods like shape-controlled catalyst synthesis method, or alloying. Also, there is still room for improvement in the fuel cell system durability, as the life time of the fuel cell system is still not comparable to internal combustion engines. During normal operating conditions, power demand variation, fuel cell start-up/shutdown cycles will cause damage to the fuel cell electrode. Some cases like hydrogen starvation will lead to severe carbon corrosion and damage the electrode in a very short time [14, 5, 3].

1.2 Background

1.2.1 Polymer Electrolyte Membrane Fuel Cells

As mentioned before, PEMFCs are electrochemical devices that convert chemical energy to electrical energy, with heat and water as the byproduct. A fuel cell system usually contains hundreds of unit cells. These unit cells are also known as membrane electrode assemblies (MEAs). Figure 1.1a shows a simplified MEA schematic. From the figure we can see that a single MEA contains two electrodes, i.e., anode and cathode, which are separated by the polymer electrolyte membrane. Each electrode contains the catalyst layer and a gas diffusion layer (GDL). The catalyst layer is where the location where electrochemical reactions happen. The GDL is a porous material made of carbon, and serves as a electrical conductor and a gas diffuse media. During normal operations, hydrogen gas is supplied to

the fuel cell anode, and air is supplied to the cathode. Gases diffuse through the GDL to each catalyst layer. At the anode catalyst surface, hydrogen gets oxidized (i.e., hydrogen oxidation reaction (HOR)) and generates electrons and protons. Since polymer electrolyte membrane is an excellent electrical insulator as well as a good proton conductor, generated protons at the anode transport through the membrane and react with oxygen at the cathode (i.e., oxygen reduction reaction (ORR)) and water is generated. Electrons will transport through the external electrical circuit to provide electrical power. The following equations can express half-cell reactions.



During the fabrication process, the catalyst material is usually coated directly on the Nafion[®] membrane or transferred to the membrane using decal transfer method, in order to create a good ionic contact between the catalyst layer and the membrane. Figure 1.2 shows the cross-sectional scanning electron microscope (SEM) image of a conventional Pt/C coated membrane.

1.2.2 Detailed Structure of the Fuel Cell Catalyst Layer

The anode and the cathode catalyst layers have similar structures. Figure 1.1b shows the detailed structure of a conventional Pt/C cathode catalyst layer. The Pt catalyst (usually 2 - 5 nm in diameter) are supported by the carbon particles (usually around 100 nm in diameter), and bounded together by the polymer electrolyte ionomer (usually Nafion[®]). The carbon support serves as the electron conductor and the Nafion[®] ionomer serves as the ion conductor in the catalyst layer. The catalyst layer is a porous structure and gas can

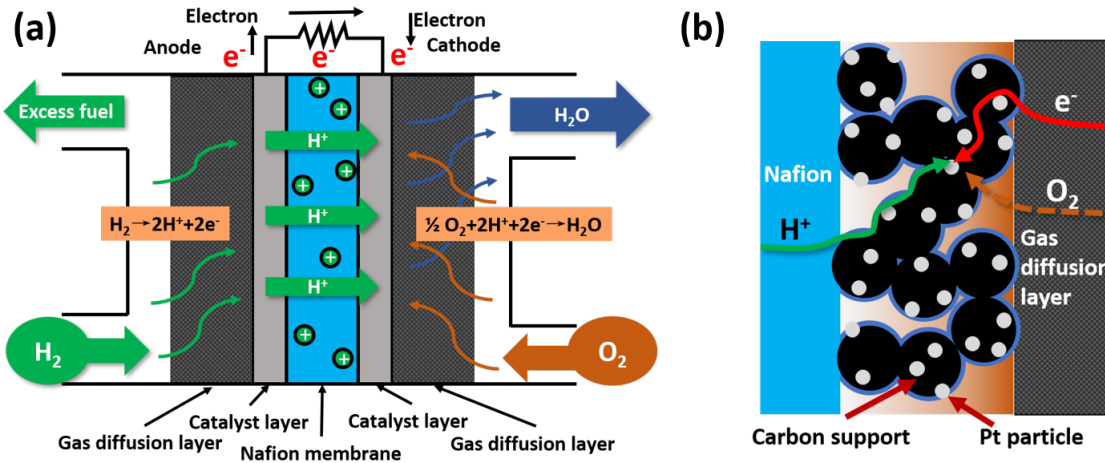


Figure 1.1: (a) The schematic of the PEMFC during regular operation. (b) A detailed structure of the cathode catalyst layer using carbon-supported platinum catalyst

diffuse through to reach the catalyst surface.

1.2.3 Pt Utilization in Fuel Cell Catalyst Layers

For PEMFCs using Pt as the catalyst, a large portion of their costs comes from the catalyst material Pt. One way to reduce the catalyst cost is to increase the Pt utilization inside the catalyst layer so that less amount of Pt is needed to meet certain power requirements. The utilization of Pt is dependent on how much of Pt is electrochemically active during the fuel cell operation. As mentioned in previous section, the Nafion[®] ionomer in the catalyst layer is the major ion conductor, and it is critical for the Pt surface to be accessible to ions in order to maintain electrochemically active. Inside the conventional Pt/C catalyst layer, there are two major types of pores, i.e., primary pores and secondary pores, which can affect the distribution of Nafion[®] ionomer and Pt. Primary pores are less than 10 nm in diameter and locate inside the carbon support particles. Secondary pores are larger in pore diameter and are caused by carbon support agglomeration. It has been found that for this kind of structure, a large portion of Pt nanoparticles are in the primary pores of

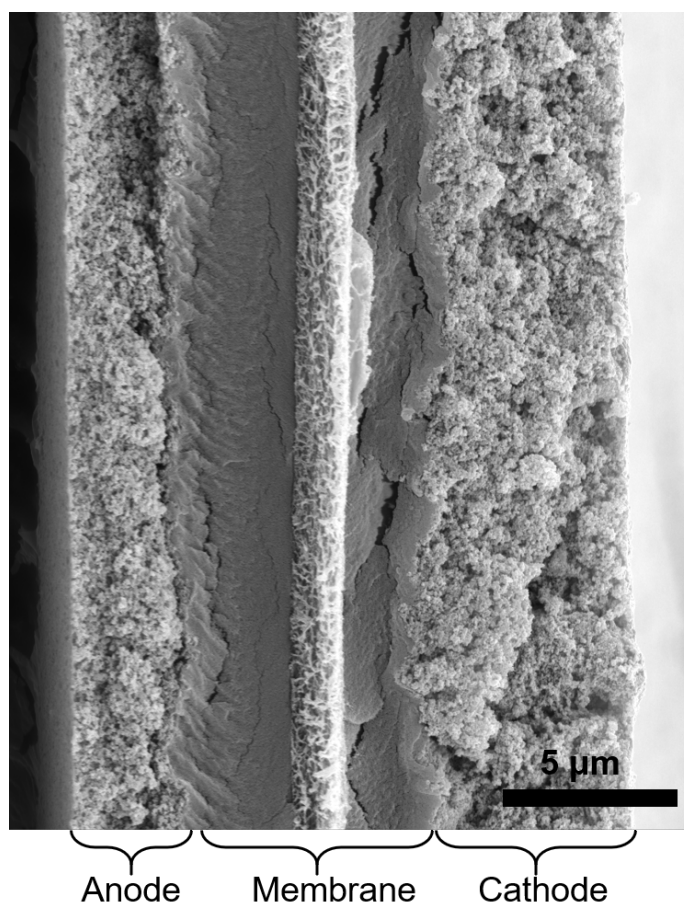


Figure 1.2: SEM image of the cross section of a conventional Pt/C catalyst coated membrane.

the carbon and cannot be directly accessed by ionic-conductive ionomer, as illustrated by Figure 1.3a. This finding is supported by the comparison of the secondary electron mode and transmission electron mode transmission electron microscope (TEM) images shown in Figure 1.3c. For Pt inside the carbon support, though not in direct contact with the Nafion[®] ionomer, it is believed that protons transport through the condensed water at the primary and secondary pores of the carbon support. Understanding the proton transport process in this water domain is critical to the improvement of Pt utilization. However, there is no sufficient study of the proton transport properties in those domains.

Another approach to reduce the amount of Pt needed in the catalyst layer is by increasing the Pt specific and mass activity using techniques like nanostructuring and alloying. One promising structure is 3M company's nanostructured thin film (NSTF) electrode [15], which has a structure shown in Figure 1.3b and SEM images in Figure 1.3d. Pt or Pt alloy is deposited on high surface area organic whiskers. This kind of electrode has no ionomer binder, lower Pt loading and higher mass activity than conventional Pt/C electrode. However, the mechanism of proton transport on this kind of electrode is also not clear.

1.2.4 Hydrogen Starvation Damage at Normal and Subfreezing Temperatures

Hydrogen fuel starvation is one of the most critical degradation mechanisms for MEAs in automotive fuel cells. Fuel cell systems usually operate at high temperatures, e.g., 65°C to 80°C. For a fuel cell system operating under normal conditions, there is HOR (Equation 1.1) at the anode and ORR (Equation 1.2) at the cathode. However, in some exceptional cases, like if there is a sudden increase in power demand, but not enough hydrogen supplied, or if liquid water is blocking the gas diffusion pathway, hydrogen starvation will occur. During hydrogen starvation, the anode potential (E_{an}) increases relative to the

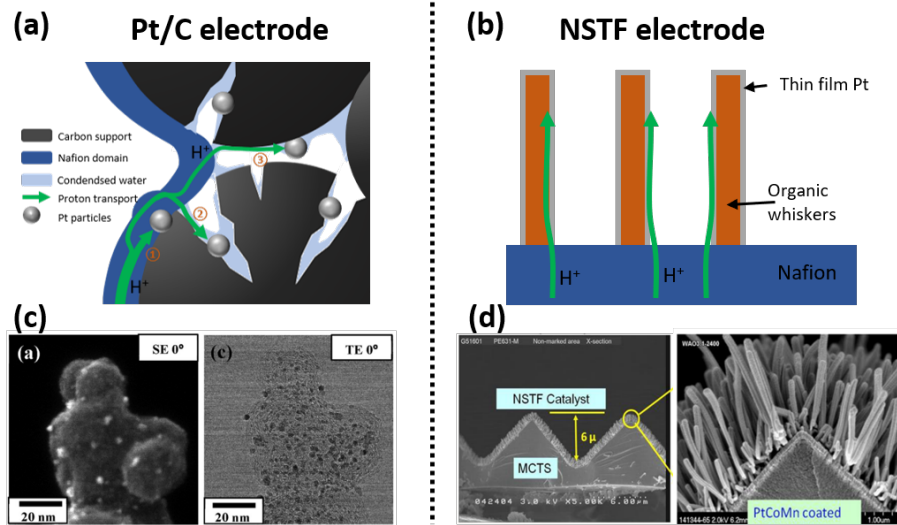


Figure 1.3: (a) Schematic of the proton transport inside catalyst layers at three different locations. 1: Pt particles covered with Nafion[®] ionomer. 2: Pt particles inside primary pores of the carbon support. 3: Pt particles in secondary pores of the carbon agglomerates. (b) Schematic of the NSTF electrode. (c) TEM images of the Pt/C electrode. Reprinted from [1], Copyright(2020), with permission from Elsevier, (d) SEM images of the NSTF electrode. Reprinted from [2], Copyright(2020), with permission from Elsevier.

cathode's potential (E_{ca}), and the cell voltage reverses ($E_{cell} = E_{ca} - E_{an} < 0$). This cell behavior is also referred to as cell reversal. During hydrogen starvation and cell reversal, the high potential at the anode leads to water electrolysis reaction (Equation 1.3) and carbon corrosion reaction (COR) (represented by Equation 1.4 and 1.5 and illustrated in Figure 1.4, high-temperature part).

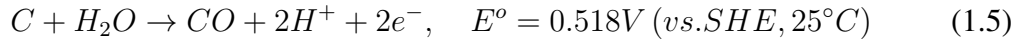


Figure 1.4b shows the cell voltage change during high-temperature hydrogen starvation. As hydrogen is cut off, the cell voltage drops to negative, plateaus around -1 V for water electrolysis reaction and then plateaus at about -1.7 V for carbon corrosion reaction. Carbon corrosion reaction can consume the essential carbon support inside the fuel cell catalyst layer, leading to structural change, Pt nano-particle agglomeration, performance loss in a very short period of time. Researchers have come up with material-based solutions to promote harmless water electrolysis reaction over harmful carbon corrosion reaction by adding water electrolysis catalyst to the anode. By delaying the carbon corrosion reaction, the fuel cell system can avoid severe degradation when hydrogen supply becomes sufficient and the fuel cell comes back to the normal operating condition. This kind of electrode is also known as reversal tolerant anode (RTA). However, it only prolongs the water electrolysis, and carbon corrosion will eventually occur [14, 5, 3] if the cell stays in hydrogen starvation for long enough time. It is believed that the failure of

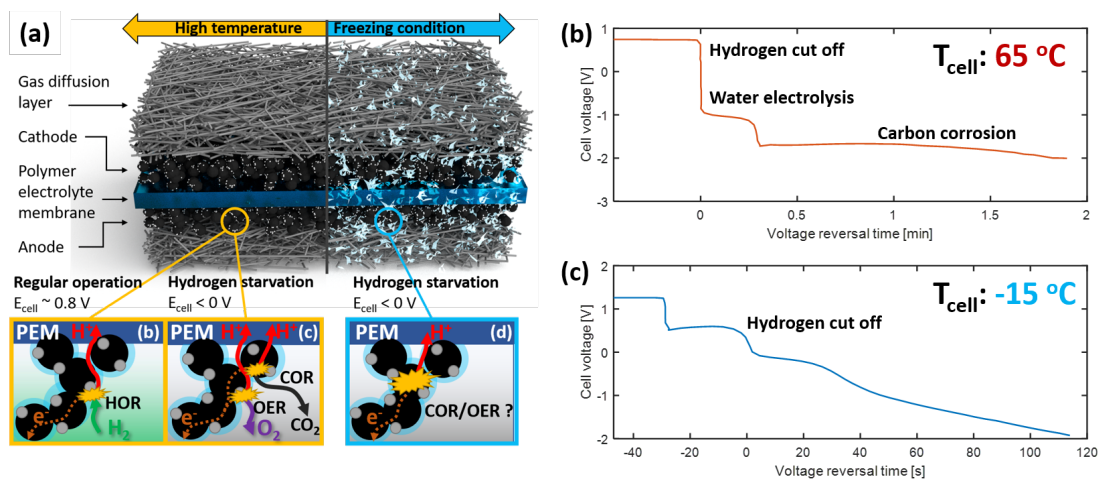


Figure 1.4: (a) Schematic of the fuel cell membrane electrode assembly and reactions at the anode at normal operating conditions, high-temperature hydrogen starvation conditions and freezing condition hydrogen starvation conditions. Reprinted with permission from [3]. Copyright (20202) American Chemical Society. (My publication) (b) Cell voltage change during hydrogen starvation at a high operating temperature. (c) Cell voltage change during hydrogen starvation at a low operating temperature.

the RTA is due to the deactivation of the water electrolysis catalyst. Though critical to the process of improving the durability of fuel cell electrodes, this water electrolysis catalyst deactivation mechanism has not been clearly understood.

Another scenario that has not been well studied is the hydrogen starvation at subfreezing conditions. It happens when there is an ice blockage in the gas flow channel or catalyst layer when fuel cell vehicle is operating in subfreezing conditions. As shown in Figure 1.4c, the cell voltage change during freezing condition hydrogen starvation is very different from that at high temperatures. Though ice blockage can be very common when fuel cell systems operating in subfreezing conditions, it is unclear if the degradation mechanism is the same as that of the high temperature. Also, if the same kind of material-based solution by adding water electrolysis catalyst will work the same way as that of high-temperature hydrogen starvation cases.

1.2.5 Start-up/shutdown Electrode Degradation

Another major issue related to fuel cell system durability is the start-up/shutdown (SUSD) degradation. When a fuel cell vehicle stops running, the remaining hydrogen gas in the anode of the fuel cell system will be replaced by air either due to intentional air purging for safety considerations or simply because of slow gas diffusion through the membrane between the anode and the cathode. When the vehicle's fuel cell system starts again, the air initially inside the anode will be replaced by hydrogen. These gas replacement processes will create a moving air/hydrogen gas boundary, as illustrated in Figure 1.5. The air/hydrogen gas boundary during SUSD will lead to uneven potential distribution in the electrolyte. In the hydrogen-rich region, the electrolyte and the anode have a minimum potential difference, due to the close to zero reversible potential of hydrogen oxidation reaction and its fast kinetics. While in contrast, in the air rich region, with the existence of oxygen, the electrolyte and the anode electrode have a high potential difference of 0.8 - 1.0

V. This will lead to a substantial potential difference between the electrolyte and the cathode electrode. High interface potential difference will lead to water electrolysis reaction and carbon corrosion reaction at the cathode, causing the shortening of fuel cell lifetime and performance loss.

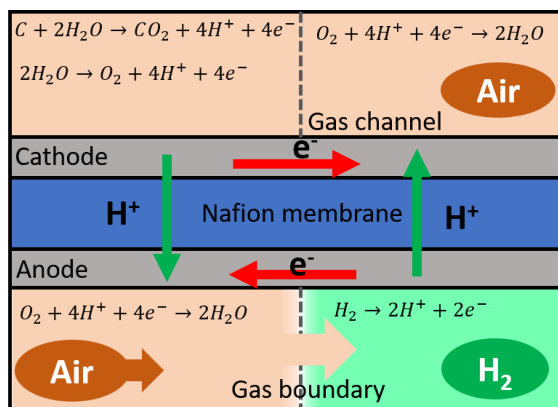


Figure 1.5: The reaction at different regions of the fuel cell with the presence of air/hydrogen gas boundary during the start-up/shut down process.

1.3 Related work

1.3.1 Proton Transport in the Ionomer-free Domain of the Catalyst Layer

Though there has already been some prior work, the proton transport mechanism is still not clear in ionomer-free electrodes (e.g., ionomer-free NSTF electrode) or ionomer-free regions within the electrodes (e.g., Pt in primary pores and secondary pores of the conventional Pt/C catalyst layer). As for ionomer-free electrodes, McBreen *et al.* [16] studied proton transport mechanism indirectly by measuring the electrochemical active surface area (ECSA) of different types of ionomer-free electrodes. Their study shows that during

cyclic voltammetry (CV) measurement, a large amount of ionomer-free Pt surfaces could still be accessed by the proton. Paulus *et al.* [17] studied the proton transport mechanism using micro-structured glassy carbon electrode with a thin Pt coating. Their results indicate that proton can transport through continuous Pt surface even with no ionomer coverage. Modeling studies by Chan and Eikerling [18] and Zenyuk and Litster [19] reveal that the Pt surface charge and the local pH have substantial effects on the ionic conductivity of metal/water interfaces. More recent works suggest that Pt surface oxide formation could actively alter the Pt surface charge [20]. Tu *et al.* [21] conducted CV measurements on Pt black microelectrode and studied the scan rate's effect on the CV results. Their work provided evidence that electrochemical reaction current density of ionomer-free Pt surfaces is strongly affected by the diffusion of adsorbed hydrogen. Thompson and Baker [22] used electrochemical impedance spectroscopy (EIS) to measure the ionic conductivity of Pt black ionomer-free electrode at a fixed bias potential of 0.2 V, showing that ionic conductivity at metal/water interfaces is several orders of magnitude higher than pure water. These previous works focused on the electrochemically active surface area but not the ORR activity. Besides, since fuel cell cathodes are working on a potential range of 0 - 1.0 V, a potential dependence study of the ionic conductivity is missing. As for ionomer-free regions of conventional Pt/C electrodes, Iden *et al.* [23] used current interrupt method and EIS for the measurement of the proton conductivity inside a pseudo catalyst layer. Gazzarri *et al.* [24] used EIS for the cathode proton transport resistance measurement. However, those works are studying the catalyst layer in the whole, not the specific ionomer-free domain, and the effect of the ionomer-free regions in the catalyst layer is indirectly investigated. Direct study of the ionic conductivity of ionomer-free region in Pt/C electrodes is still missing.

1.3.2 Fuel Cell Degradation Related to Hydrogen Starvation and Reversal Tolerant Anodes

Many efforts have been made regarding the effect of hydrogen and cell reversal to the cell performance at high temperatures, i.e., 60 - 90°C [14, 5, 3, 25, 26, 27]. Taniguchi *et al.* [28] used reversible hydrogen reference electrode to study the anode and cathode potential change during reversals at 80°C. The spatial distribution of electrode degradation was also investigated. Liang *et al.* and Liu Taniguchi *et al.* used segmented cell technique to study the uneven voltage and current distribution during hydrogen starvation and cell reversal. Hong *et al.* conducted cell reversal tests at 90°C with different relative humidities and showed that the performance of the RTA made from iridium oxide (IrO_2) is low at both water-deficient and water-excess conditions. This behavior is attributed to the competing behavior between water electrolysis and carbon corrosion reactions under given relative humidity conditions. Recently, You *et al.* [26] examined the effectiveness of iridium ruthenium alloy with carbon support (IrRu_4/C) RTA and proved that it could increase the anode durability during cell reversal at high temperature conditions. Though many research works have been done on high-temperature hydrogen starvation and cell reversals, there are few works conducted on studying freezing condition hydrogen starvation and cell reversals.

1.3.3 Fuel Cell Degradation Related with Start-up/shutdown Process

As for start-up/shutdown degradation mechanism, Reiser *et al.* [29] used numerical and experimental method and showed that a reverse current would appear during the start-up/shutdown cycle and the membrane ionic potential change at the gas boundary is the leading cause of the carbon corrosion at the cathode. Park *et al.* [30] used potential cycling to simulate the potential change at the cathode during start-up/shutdown and found

that Pt can accelerate the carbon corrosion process. Ishigami *et al.* [31] used specially designed fuel cell hardware to visualize the change of the air/hydrogen boundary during the start-up/shutdown process and found that there is a big difference of the actual gas replacement time and the theoretical one, the slow gas replacement time is attributed to the consumption of oxygen caused by the cathode side corrosion. There are many mitigation methods regarding the start-up/shutdown damage [32, 33]. Durst *et al.* [34] are the first to show the effectiveness of carbon-supported Ir (Ir/C) as the selective anode and reduce the start-up/shutdown damage. Selective anode approach is considered as the most promising material-based solution.

1.4 Methods

1.4.1 Electrochemical Characterization Methods

Polarization curve measurements

Polarization curve can be obtained by measuring the cell voltage at different current densities or by controlling the voltage and measuring the current density. During the polarization curve measurement, the anode is supplied with hydrogen and the cathode is supplied with air or oxygen. A typical polarization curve can be shown in Figure 1.6. The reversible potential for ORR at the standard condition is 1.229 V vs. standard hydrogen electrode (SHE). The shape of the polarization curve is dominated by the variation of different losses at different current densities. At low current densities, the activation loss is dominating, which is basically the voltage penalty for the electrochemical reaction to happen at certain speed. The HOR has very fast reaction kinetics and the anode activation loss is relatively small, and the ORR has a slower reaction kinetics and contributes to most of the activation loss. The Ohmic loss can be described by the Ohm's law ($\Delta V_{\text{Ohm}} = I \times R$), where R is

the high-frequency resistance and mainly comes from the membrane ionic resistance and the contact resistance. The ohmic loss increases with the current density. At high current densities, the mass transport loss becomes significant, and it results from the decrease in the reactant concentration at the surface of the electrode as reactant is consumed faster at higher current densities. We can get a lot of useful information from the polarization curves, including the general performance of an electrode, the extent of degradation. Polarization curve measurements are used in Chapter 2 for electrode performance study at different relative humidities (RHs) and Chapter 5, 6 and 7 for the electrode degradation studies.

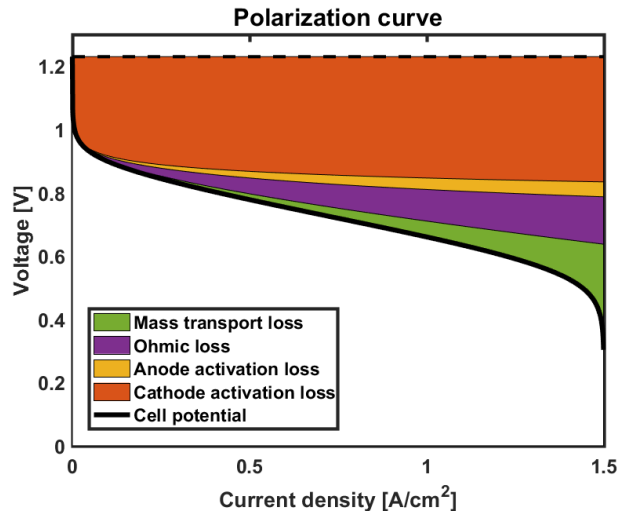


Figure 1.6: A typical polarization curve and different losses.

Cyclic voltammetry curve measurements

CV is an effective method that is used to obtain fuel cell catalyst layer ECSA, and other useful information. During CV measurements, the anode is supplied with hydrogen, and the cathode is supplied with air. The test station configuration is shown in Figure 1.7a. A linearly sweeping voltage is applied to the cell in a certain voltage window, as shown in Figure 1.7b. The typical cathode CV response of a fuel cell with conventional Pt/C

catalyst layer is shown in Figure 1.7c. The minimum current response in the potential range from 0.4 to 0.6 V is caused by the electrical double layer charging. At low potentials, for Pt catalyst, there are hydrogen adsorption and desorption surface reactions, and at high potentials, there are surface oxide formation and reduction reactions. By calculating the charge transferred during hydrogen adsorption or desorption process, with the electrical double layer current subtracted, we can calculate the ECSA of the electrode. Other information like the hydrogen crossover current, unusual peaks can tell us the state of health of the fuel cell. CV curve measurements are used in Chapter 2 for electrode ECSA study at different RHss and Chapter 5, 6 and 7 for the electrode degradation studies.

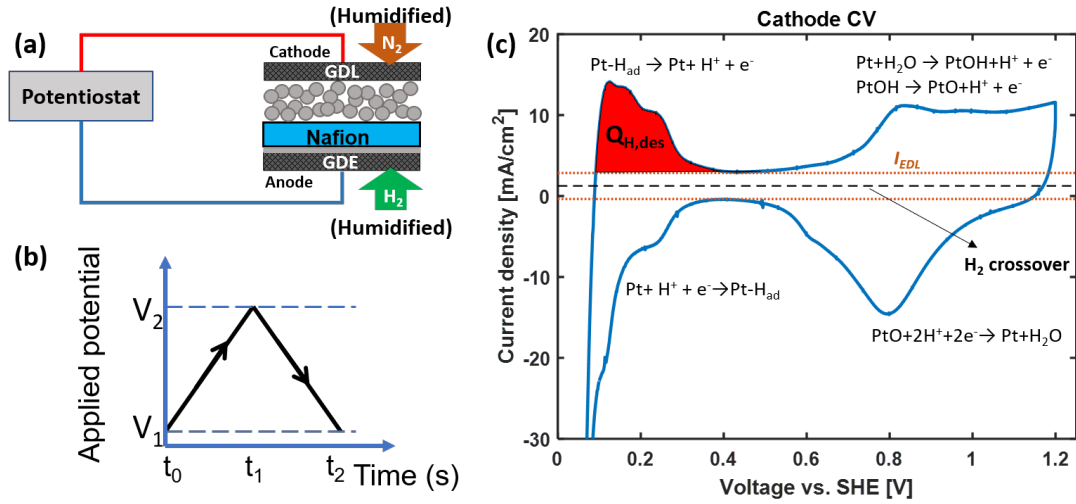


Figure 1.7: (a) Test stand configuration during CV measurements. (b) The voltage profile for CV measurement. (c) A typical CV curve for Pt/C catalyst in hydrogen/nitrogen environment.

Electrochemical impedance spectroscopy measurements

Figure 1.8a shows the EIS measurement process. During the EIS measurement, the cell is operated in certain conditions and a very small current or voltage perturbation is applied to the cell. The corresponding voltage or current response to that perturbation is mon-

itored and analyzed. With a wide range of different frequency sine wave perturbations, a fuel cell MEA can usually be modelled as an equivalent resistor-capacitor (RC) circuit using membrane ionic resistance (R_m), anode/cathode charge transfer resistance (R_{an} and R_{ca}) and double layer capacitance (C_{an} and C_{ca}). The membrane ionic resistance is the resistance value obtained at high frequency (usually > 1 kHz). In a typical EIS Nyquist plot, as shown in Figure 1.8b, the charge transfer resistance and the electrical double layer capacitance in parallel are shown in the shape of semi-circles. From the membrane ionic resistance, we can calculate the ohmic losses of the fuel cell. From the charge transfer resistance, we can get information about the catalyst layer performance and degradation information. EIS measurements are used in Chapter 3 for carbon/water interface ionic conductivity study at different RHs, and in Chapter 5, 6 and 7 for the electrode degradation studies.

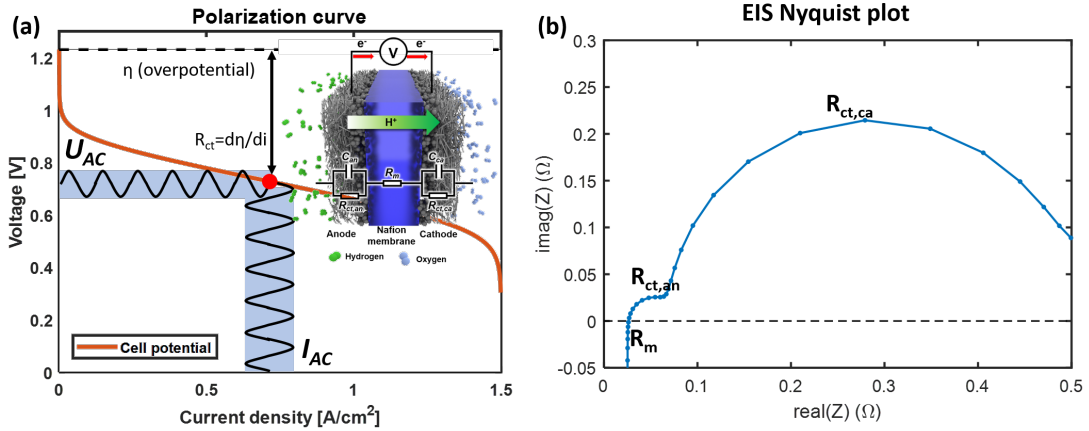


Figure 1.8: (a) Schematic illustrating the EIS measurement process. (b) A typical Nyquist plot of the an EIS measurement.

1.5 Scope of Thesis

This dissertation discusses the proton transport properties at ionomer-free domains of catalyst layers in PEMFCs. It also presents studies related to durability of the PEMFC electrodes, specifically hydrogen starvation induced damage and start-up/shutdown cycle induced damage. This dissertation contains 9 chapters. The first chapter is a general introduction about background of each topic, method used for each study and related existing researches. Chapter 2 presents the study on proton transport properties at metal/water interfaces, which is related to the recently emerged ionomer-free NSTF electrode. Chapter 3 explores the proton transport properties at the carbon/water interfaces, which is related to Pt utilization in conventional Pt/C catalyst layers. Chapter 4 is about the deactivation mechanism of the water electrolysis catalyst in RTA. Chapter 5 presents the hydrogen starvation in subfreezing conditions and its effect to the fuel cell durability. Chapter 6 is about the new anode structure, reversible invincible anode, that can largely improve the fuel cell anode durability. Chapter 7 is about the exploration of different anode catalysts and their effect on fuel cell's start-up/shutdown durability. Chapter 8 is about the summary of conclusions, contributions and potential future works. Appendix B is about the segmentation method that is developed for the catalyst layer morphology study. Appendix C presents some of the preliminary results on integrating diode to the fuel cell to prevent hydrogen starvation damage. Appendix D is about the preliminary results on temperature sensing in during freezing reversal tests.

Chapter 2

Proton Transport at Metal/Water Interfaces

2.1 Introduction

This chapter presents the study of proton transport properties at metal/water interfaces. As mentioned in section 1.2.2, the novel nanostructured thin film (NSTF) electrode are promising because of its high mass activity as well as high specific activity [15]. This kind of electrode has platinum (Pt) thin films with organic whiskers as the support, as shown in Figure 2.1a. The NSTF does have Nafion[®] thin film as the catalyst layer electrolyte, as shown in Figure 2.1b. However, the proton transport mechanism is not clear. Based on previous researches, two proton transport mechanisms have been proposed. The first is that proton gets adsorbed to Pt surface and diffuses along the Pt surface, as shown in Figure 2.1c. The second is that proton can migrate through the electrical double layer formed at the water film on the Pt surface, as shown in Figure 2.1d. Two metal surfaces are studied, Pt and gold (Au). Polarization curve and cyclic voltammetry (CV) measurements were conducted at different relative humidity (RH)s to examine the RH dependence of the proton transport properties. A specially-designed micro-structured electrode scaffold

(MES) device was used for the four wire ionic conductivity measurement (MES method was developed by our group and previously reported in [35, 36]). The potential and RH dependence of the ionic conductivity of ionomer-free Pt and Au electrode were examined using MES. Some results presented in this chapter were previously published in [4].

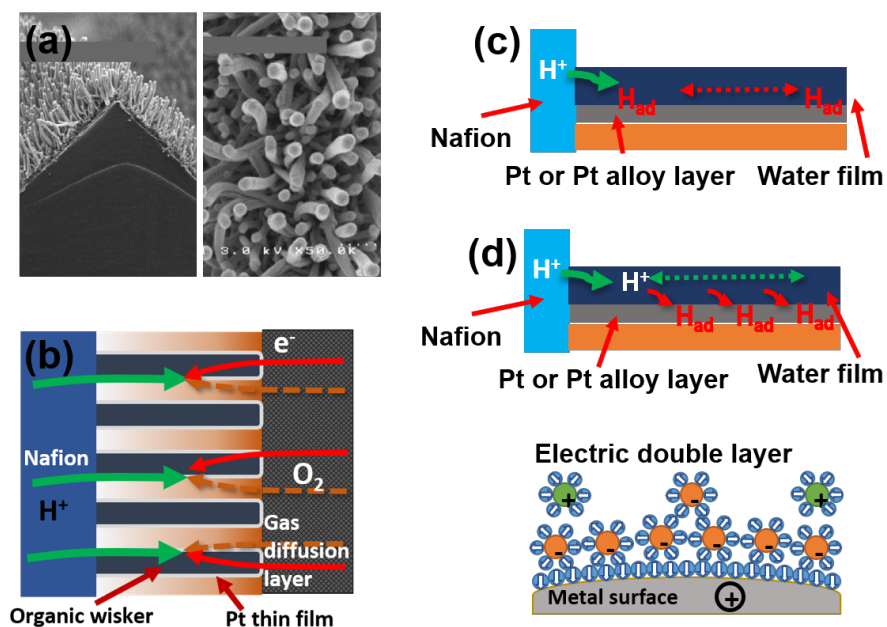


Figure 2.1: (a) SEM image of the NSTF electrode. Reprinted from [2], Copyright(2020), with permission from Elsevier. (b) A detailed structure of the NSTF electrode during ORR. (c) Illustration of proton surface diffusion. (d) Illustration of proton migrate through electrical double layer.

2.2 Experimental

2.2.1 MEA fabrication and electrochemical characterization

Figure 2.2 presents the structure of the membrane electrode assembly (MEA) for the characterization of Pt and Au ionomer-free electrodes as well as a Pt electrode containing

ionomer. The materials used for this study is fuel cell grade Pt black (95+%, HiSPEC 1000, Johnson Matthey Fuel cells, Swindon, UK, 6.5 nm, surface area 24 m²/g) and Au micro particles (average particle size (APS) 0.5-0.8 μm, 99.96+%, Alfa Aesar, Haverhill, USA). The anode and cathode gaskets has opening area of 1 cm² and 5 cm² respectively and are made of Kapton[®] (25 μm thickness, McMaster-Carr, Aurora, USA). A Nafion[®] membrane (Nafion[®]211, Ion Power, New Castle, USA) was used in between electrodes. The anode was made of commercial gas diffusion electrode (GDE) (0.3 mg/cm² 40% Pt on Vulcan carbon paper, Fuel Cells Etc., College Station, USA). The ionomer-free catalyst inks were prepared by adding Pt black or Au micro particles into isopropanol (IPA) containing 50 vol.% of IPA. The Pt black catalyst ink with ionomer has the same formulation but with extra Nafion[®] (D521, IonPower, New Castle, DE) solution added drop by drop to achieve an ionomer to catalyst ratio of 0.6:1. Prepared catalyst inks were magnetic stirred for 30 min and ultra-sonicated for another 3 min before painted on the cathode gas diffusion layer (GDL). The catalyst loading was 15.0 mg/cm² for Au cathode. The Au cathode has an estimated thickness of 16 μm of thickness with an estimated porosity of 0.5. The catalyst loading for Pt black cathode was 17.0 mg/cm². The Pt black ionomer-free cathode has an estimated thickness of 16 μm of thickness with an estimated porosity of 0.5.

A commercial fuel cell testing stand (FCT-150 S, Bio-Logic, Claix, France) was used to control experiment parameters like cell temperature, RH, and gas flow rates. The CV and polarization curves were measured with a potentiostat (VSP, Bio-Logic, Knoxville, TN, USA). As for the study of the influence of water on the ionic conductivity, the RH was varied in the range of 70%, 80%, 90%, 100%, 110%, and 120%. It should be noted that RH above 100% indicates that the electrode is over-saturated, and the gas has a dew point higher the fuel cell temperature. For the CV measurement, the cell temperature was 60°C and the gas flow rates for the anode (hydrogen (H₂)) and the cathode(nitrogen (N₂))

are both 400 ml/min. The high temperature was used for CV measurement in order to provide enough humidifier dew point temperature range for the RH variation. The CV measurement was conducted by linearly sweeping the cell voltage between 0.0 and 1.5 V with a scan rate of 40 mV/s. For the cell polarization curve measurement, the gas flow rate, cell temperature, and RH range were the same. But the cathode gas was air for oxygen reduction reaction (ORR) reaction. The high-frequency resistance of the cell was obtained after the end of each potential hold during the polarization curve measurement using electrochemical impedance spectroscopy (EIS). The CV and polarization curve measurements were conducted at ambient pressure, and polarization curve measurements were repeated three times at each testing condition.

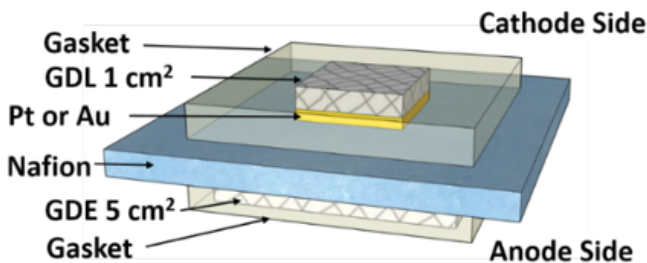


Figure 2.2: Schematic of the MEA for electrochemical measurement. The upper part represents the cathode and the lower part represents the anode. The cathode consists of a 1 cm² layer of Pt or Au and GDL, and the anode is made of a 5 cm² GDE. Reprinted from [4], Copyright(2020), with permission from Wiley.

2.2.2 MES fabrication and ionic conductivity characterization

The MES device was used for the ionic conductivity measurement. The configuration is shown in Figure 2.3a. It contains a stack of alternating Kapton[®] insulating films (25 μ m thick) and Nafion[®] as the electrolyte bridges. Two different types of Nafion[®] films were used for Au and Pt electrodes, respectively. For the Pt ionomer-free cathode, Nafion[®]

sensing layers were fabricated using spin coating method. Nafion[®] solution (D2020, 20wt%, IonPower, New Castle, DE) was used for the coating on both side of the Kapton[®] film. The final coated Nafion[®] has a thickness of approximately 2 μm per layer. The coated Kapton[®] films were then stacked and hot-pressed at 690 kPa and 125°C for 8 mins to achieve good binding between Nafion[®] layers. A cylindrical cavity with a diameter of 200 μm and a depth of 415 μm was made by micro-drilling (Model 214 tabletop precision micro drill press, Camero, Sonora, CA). After that, an extra Nafion[®] 115 membrane was hot pressed to the bottom of the stack, with the same hot pressing condition. The created cavity was then hand-filled with Au or Pt catalyst. A GDL was placed on top of the cathode cavity. A GDE was used as the anode. Finally, eight hydrogen reference electrode (HRE)s made from the same GDE were placed on the end of each protruding tab of the Nafion[®] sensing layer with the custom hardware shown in Figure 2.3b.

The layered structure in MES was used to conduct the four-wire conductivity measurement, as shown in Figure 2.3a. During the measurement, the anode was supplied with H₂ and the cathode was supplied with N₂, with gas flow rates of 200 ml/min at both electrodes. The cathode RH was varied between 85%, 95 %, 100 %, and 120 %. For cases that cathode RH was below 100%, the anode RH was set to be the same as the cathode. When the cathode RH was above 100%, the anode RH was set to be 100%. The cathode potential was controlled between 0 - 0.9 V for RH dependence studies and 0.2 - 1.3 V for potential dependence studies.

As mentioned before, the MES was placed in a custom hardware with eight HREs. Each HRE has its own H₂ supply channel and a current collector made of graphite, which is connected to a printed circuit board (PCB) as shown in Figure 2.3b. As shown in Figure 2.3a, the four-wire measurement has one potentiostat channel controlling the cathode potential relative to the anode. A second potentiostat channel was connected to the Nafion[®] sensing layer through the HRE to pass through hydrogen pumping current. The hydrogen

pumping current has a perturbation that was controlled to be sufficiently small so that the applied cathode voltage was not notably affected. The voltage response caused by the current perturbation was sensed between other two HREs. Figure 2.3c presents a typical current interrupt and the corresponding voltage response. The ionic resistance of the ionomer-free cathode and conductivity can be calculated using Equation 2.1 and Equation 2.2, respectively.

$$R = \frac{\Delta I_{H_2}}{\Delta V_{H_2}} \quad (2.1)$$

$$\sigma = \frac{L}{R \cdot S} \quad (2.2)$$

where in Equation 2.2, S is the area of cross-section of the ionomer-free catalyst cylinder. L is the thickness of the cylindrical cathode between the voltage sensing leads. ΔI_{H_2} is the applied perturbation current and ΔV_{H_2} is the corresponding voltage response.

2.2.3 Water uptake characterization

Since relation between the cathode RH and the water uptake is not linear, it is important to quantify the amount of water at the cathode surface at different RHs. A volumetric method was used with a specially-designed vapor adsorption apparatus at Giner Inc, MA.

2.3 Results and Discussion

2.3.1 CV and polarization curves for the Au cathode

Figure 2.4a shows the CV curves of the Au cathode at different RH conditions. In acidic environments, there are oxide species formation/reduction on the Au surface and can be

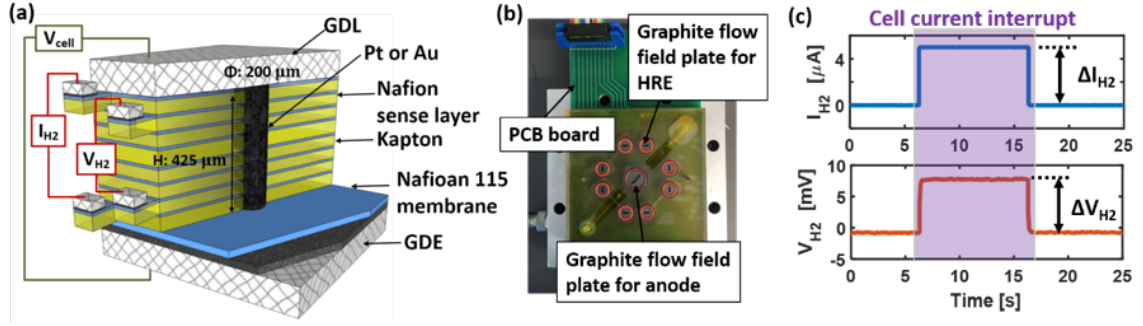
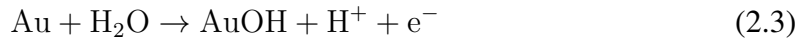


Figure 2.3: (a) Schematic of the MES for measuring Pt or Au ionomer-free cathode's ionic conductivity. The Pt or Au ionomer-free catalyst layer has a diameter of 200 μm . (b) Photo of the MES experiment hardware. In the center, there is the graphite flow field plate for the anode and around it, there are eight graphite flow field plates for HREs. (c) A typical voltage response during the current interrupt, where the ΔI_{H_2} is the applied interrupt current and the ΔV_{H_2} is the measured voltage response. Reprinted from [4], Copyright(2020), with permission from Wiley.

expressed by Equation 2.3 and Equation 2.4, which are shown as characteristic peaks in CV curves at around 1.2 V [37, 38].



From the CV curves, we see that capacitive current caused by electrical double layer (EDL) (in the potential range 0.3-0.8 V) increases with the cathode RH. Increasing the RH also results in increased anodic peak current density representing the Au oxide formation/reduction. The corresponding high frequency resistance (HFR)-free polarization curves for the Au ionomer-free cathode show the impact of RH on the ORR current den-

sity in Figure 2.4b. ORR current densities are low at 70% and 80% RH, which is possibly due to low active surface area under these dry conditions. The current density of ORR increases significantly starting from 90% RH and is commensurate with the increased active surface area shown in curves of the CV. Interestingly, the current rise is approximately proportional to the increase in EDL current seen in Figure 2.4a, when compare the current density at 70%, 90% and 120% RH at 0.2 V. It should be noted that the polarization curve is not significantly affected by mass transport losses due to low ORR activity of Au in acidic environment. These results suggest that in Figure 2.4b, the observed current is activation-limited, which scales at a given voltage with the active catalyst surface area.

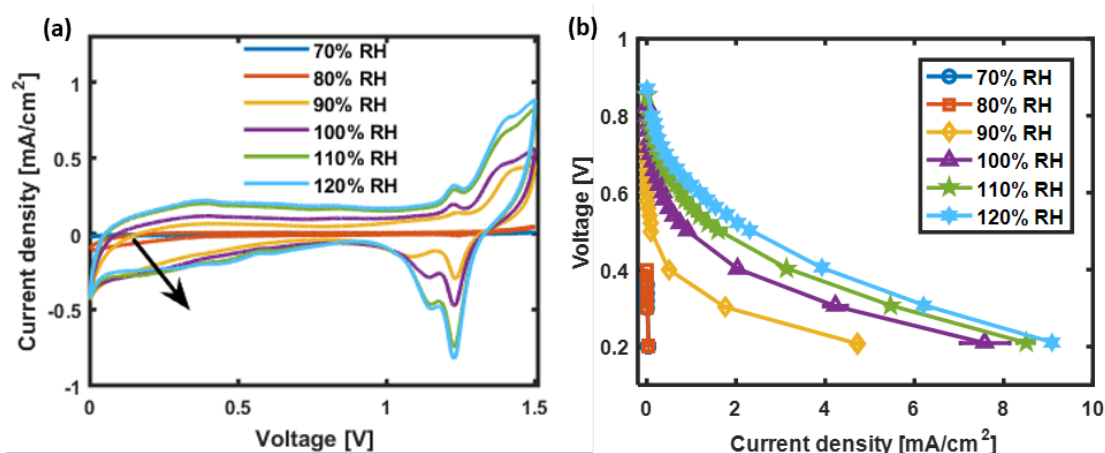


Figure 2.4: CV and polarization curve characterization results of the Au cathode at six different RH conditions. (a) CV curves. (b) Polarization curves. Reprinted from [4], Copyright(2020), with permission from Wiley.

electrochemically active roughness factor (ECRF) can be defined as the catalyst's electrochemical active surface area (ECSA) divided by the electrode's geometric surface area, as shown in Equation 2.5. The ECSA of the Au electrode is obtained by integrating the oxide reduction peak's charge from the CV curves. To convert the charge to active surface

area, a reference value of 0.386 mC/cm² [39]

$$ECRF = \frac{A_{Active}}{A_{Geo}} \quad (2.5)$$

Figure 2.5 shows the ECRF and ORR current densities of Au at different RH conditions. Current densities at 0.8, 0.6 and 0.3 V are chosen to reflect the activation, ohmic and mass transport limited region in the polarization curves. The ECRF values are small in dry conditions. The ECRF is 0.0168 cm²_{Au}/cm² at 70% RH and is 0.0264 cm²_{Au}/cm² at 80% RH, respectively. It should be noted that the current densities from polarization curves at the same RH conditions are also small. When the RH was increased to 90%, there is a substantial increase of the ECRF to 1.95 cm²_{Au}/cm². Further increase in the RH from 90% to 120% leads to an increase of 242% in the ECRF value to 6.69 cm²_{Au}/cm². This suggests that a larger Ausurface area that is accessible by protons in the more hydrated environment. The increase of current densities at different voltages follows the trend of the ECRF closely and commensurates with percolating water coverage. At 70% RH, the nearly complete loss of ECRF indicates a limited surface area are active, probably corresponds to Au surface area adjacent to the Nafion[®]/Au interface.

2.3.2 CV and polarization curves for the Pt cathode

Figure 2.6a presents Pt black cathode's CV curves. We can see that the capacitive current at the EDL region (0.4 -0.6 V) increases by 150% from 70% to 120% RH. The hydrogen adsorption and desorption current densities for Pt black cathode become higher as the RH increases. Both of these trends suggests that a larger surface area is electrochemically active at higher RHs. As the RH increases to 110% and 120%, CV curves start to overlap, indicating that the cathode reaches its maximum ECRF.

Figure 2.6b shows the Pt black cathode's polarization curves at a variety of RH con-

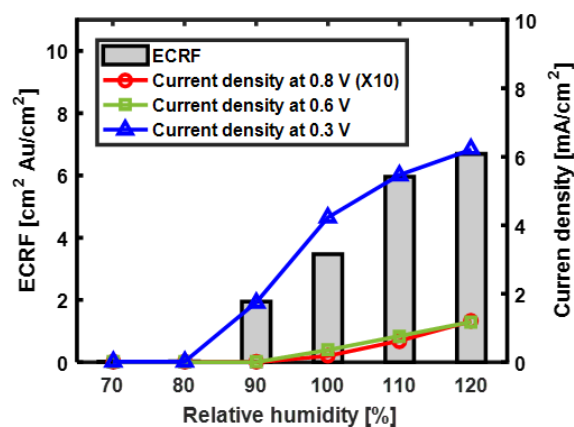


Figure 2.5: ECRF and current densities of the Au micro-powder cathode at different RH conditions. Current densities at 0.8 V, 0.6 V and 0.3 V are presented. For convenience of visualization, the value of current densities at 0.8 V are multiplied by 20, and the value of current densities at 0.6 V are multiplied by 4. Reprinted from [4], Copyright(2020), with permission from Wiley.

ditions. At cell voltage of 0.8 V or higher, i.e., the activation loss dominated region, we can see that the current density increase with the RH. As the RH increases to 100% or higher, the mass transport loss becomes significant, as shown by the current decrease at cell voltage below 0.8 V. The increased mass transport loss is caused by the liquid water accumulation and flooding at the cathode. The excess water comes from the product of ORR and the flooding is severe for Pt electrode as the current density is much higher at certain cell voltages compared with the Au cathode. It has been previously shown that this phenomenon can be alleviated by adding hydrophobic binders like polytetrafluoroethylene [40, 41, 42].

Figure 2.6c shows the comparison of the CV curves of Pt black electrode with ionomer and without ionomer. From the CV curves, we can see that the Pt black cathode with ionomer shows negligible RH sensitivity. In comparison, the CV curves of the Pt black

ionomer-free electrode shows significant differences between 80% and 100% RH, indicating a change in the amount of percolating water coverage. The corresponding Tafel plots are shown in Figure 2.6d. From the Tafel plots comparison, we can see that the Pt black cathode with ionomer show insignificant change in activity when the RH is changed from 80% to 100%. However, the ionomer-free Pt black electrode is more sensitive to RH changes.

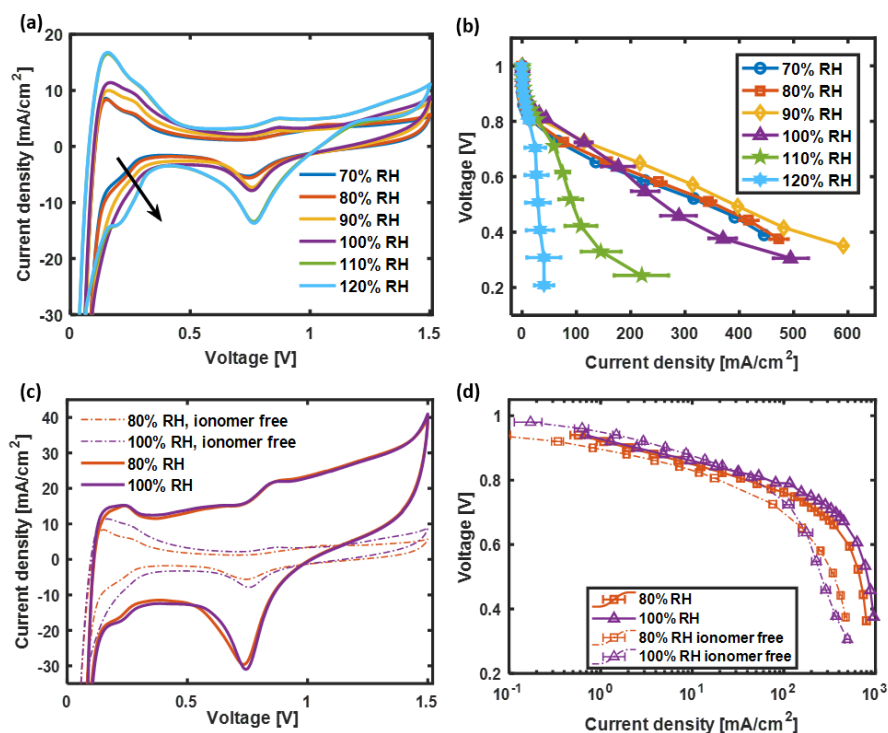


Figure 2.6: Characterization of the Pt black cathode at six RH conditions. (a) CV measurements with voltage scans from 0 V to 1.5 V with a scan rate of 40 mV/s. The arrow stands for the direction of RH increase. The 110 and 120% curves are overlapping. (b) Polarization curves. (c) CV comparison between Pt black electrodes with and without ionomer and (d) Tafel plots of Pt black electrodes with and without ionomer at 80% RH and 100% RH. Reprinted from [4], Copyright(2020), with permission from Wiley.

Figure 2.7a presents the water uptake measured at different RH conditions. The ad-

sorption isotherms were measured in N₂, H₂ and air environments. Isotherms measured in air and N₂ environment provide the water uptake on Pt with its surface covered with oxide. The isotherm obtained in H₂ environment provides the water uptake information on Pt with an oxide-free surface. The oxidized Pt surface (in N₂ and air environment) adsorb more water compared with the oxide-free surface in the RH range of 10% to 80%, which could be attributed to the more hydrophilic surface with oxide. In all three gas environment, a steep increase in water uptake happens when the RH increases above 80%. The steep increase of water uptake suggests pore-filling water condensation inside the porous electrode at high water vapor partial pressure. Different from the Au electrode, which has a mean particle diameter of 0.5-0.8 μm , the Pt black has a much smaller mean particle diameter of 6.5 nm, suggesting a mesoporous electrode structure. Figure 2.7 shows the variation of the ECRF and the current density with RH. The Pt black electrode's active surface area can be obtained by integrating the charge transferred during the hydrogen desorption process (voltage range 0.08 - 0.4 V) of CV curves [43]. To convert the charge transferred to active surface area, a reference charge density value of 210 $\mu\text{mC}/\text{cm}_{\text{Pt}}^2$ is used [44]. From the plot we can see that the ECRF value at 80% RH is about half of that at 100% RH. Figure 2.7b also shows the current density at different cell voltages and different RHs. Current density values at each cell voltage are normalized based on the current density value at 70% RH of that specific cell voltage. The normalized current densities at 0.92 and 0.9 V are activation loss dominated and keep increasing as the RH increases, following the same trend as the ECRF. At 120% RH, current densities at 0.92 and 0.9 V start to drop, which could be attributed to severe water condensation in the catalyst layer and blockage of the gas diffusion channels. At lower cell voltages, the increase of current densities follow the trend of the ECRF. Since there is larger amount of water generation due to ORR, the impact of electrode flooding becomes more dominant. The consistency of the ORR current density and the ECRF with RH indicates that the same proton trans-

port mechanism supporting the current in the CV measurement also supports the proton transport for the ORR in the cathode.

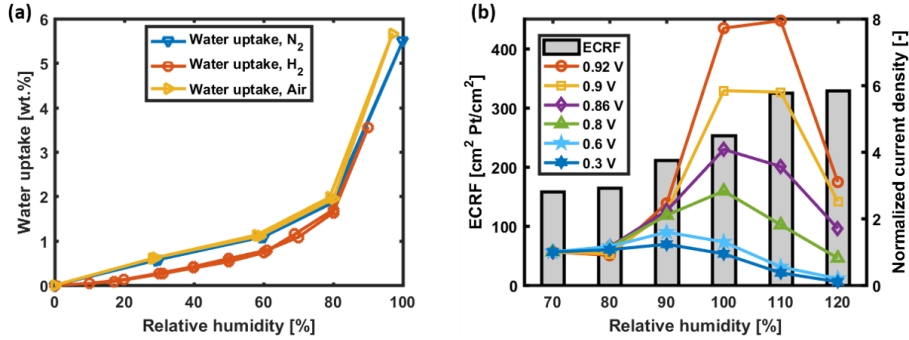


Figure 2.7: (a) Adsorption isotherms of water on the Pt black catalyst powder. (b) ECRF and current densities of the Pt black cathode at different RH conditions. The current density values were normalized based on the corresponding value at 70%. Reprinted from [4], Copyright(2020), with permission from Wiley.

It should be noted that, based on calculation, a high ECRF value of 300 cm²_{Pt}/cm² is reached at high RH conditions. Given that the Pt black has a specific surface area of 30 cm²_{Pt}/g, the high ECRF suggests that more than 1 μ m thickness of the electrode are accessible to proton during the CV measurement. This thickness is much higher than the Debye length (i.e., the nominal electrical double layer thickness) at the Nafion[®]/water interfaces, indicating that the Pt surface is facilitating proton transport over significant distances. As for the Au electrode, if we assume an average 0.7 μ m particle diameter, the specific surface area for the Au electrode is 0.44 cm²_{Au}/g. The measured maximum Au ECRF of 6 also indicates that Au surface more than 1 μ m from the Nafion[®]/water interface is accessible to proton during the CV measurement. The difference in the ECRF's RH-dependency of Pt and Au electrode is likely to be caused by the difference in their water uptake. Since the Pt electrode is mesoporous, while the Au electrode has much larger pores.

2.3.3 Ionic conductivity of Au and Pt ionomer-free electrodes

In previous sections, the variation of ECRF and polarization curves at different RHs provide correlations among the water uptake, the proton accessible Pt and Au surface area, and the ORR activity. However, no direct measurement of ion transport properties is given. The ionic conductivity within the ionomer-free porous electrode can be affected by the metal surface's water coverage, connectivity, as well surface charge. It is generally believed that the metal surface charge can be balanced by the excess ion in the electrolyte. Meanwhile, the metal surface charge is dependent on the electrode's potential, the potential of zero charge (PZC) and metal surface's oxide induced dipoles. This section will present the proton conductivity at the metal/water interface obtained using the MES method.

Figure 2.8a shows the ionic conductivity of Au and Pt ionomer-free electrode at different electrode potentials at 120 % RH. From the plot, we can see that the ionic conductivity of the Au electrode shows a minimum of 0.043 S/m at 0.9 V. The highest ionic conductivity is 0.23 S/m at 0.2 V, which is 5 times larger compared with the minimum value at 0.9 V. Figure 2.8b presents each individual measurement from high to low or from low to high electrode potentials. The potential dependence in each individual potential sweep is more notable compared with the averaged values in Figure 2.8a. The potential dependence of the ionic conductivity is consistent with the classical EDL theory and proton conduction in the EDL. Given the clean and idea surface of Au at this potential range, this potential dependence is expected. The ionic conductivity should be minimum at round the effective PZC of the Au surface, based on the classical Gouy-Chapman-Stern EDL model [45, 46, 47]. The electrode potential of 0.9 to 1.0 V versus HRE where the minimum ionic conductivity is located, is consistent with the Au PZC reported in other researches [48, 49]. When electrode potential is below the PZC, there are excess negative charges at the metal surface, results in increase of cations (protons) in the EDL. As the potential

increases to be higher than the PZC, similarly, ion concentration in the EDL increases and yields roughly proportional increase in conductivity as we observed.

Different from the Au electrode, the ionic conductivity of the Pt electrode show less notable dependence on electrode's potential, and the ionic conductivity is relatively constant over the potential range. As Figure 2.8c shows, each individual test shows no clear trend with respect to the direction of the potential dependence test. These observations suggest that the proton or hydrogen transport on the Pt surface can not be explained by the Guoy-Chapman-Stern model.

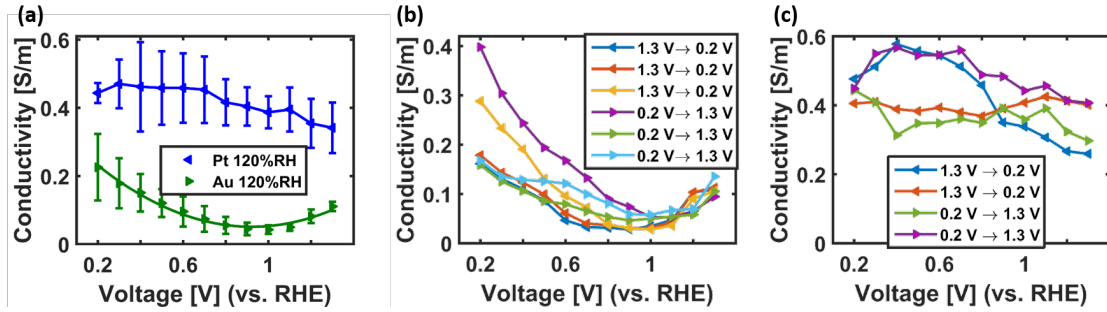


Figure 2.8: (a) Comparison of ionic conductivity for Pt black and Au ionomer-free electrodes measured by MES method. (b) Individual measurement of ionic conductivity for the Au electrode. (c) Individual measurement of ionic conductivity for Pt black electrode with different measuring sequence. Reprinted from [4], Copyright(2020), with permission from Wiley.

Figure 2.9 shows the ionic conductivity of the Pt electrode at a variety of RH conditions, with electrode potential changing from 0.1 to 0.9 V vs. reversible hydrogen electrode (RHE). The ionic conductivity of 0.21 S/m at 0.2 V and 100% RH is comparable to the previously reported value measured using EIS [35]. Though the proton transport is highly dependent on surface water, the observed ionic conductivity is much higher than bulk water, suggesting an increased ion concentration at the metal/water interface. The

ionic conductivity of Pt electrode increases with RH over the whole potential range. From 85% to 120% RH, the measured ionic conductivity increases from 0.024 S/m to 0.46 S/m. It should be noted that the increase of the measured ionic conductivity is not linearly related to the RH. The increase of the ionic conductivity is more significant from 95% RH to 100% RH than from 85% RH to 95% RH, consistent with the change of water uptake with the RH.

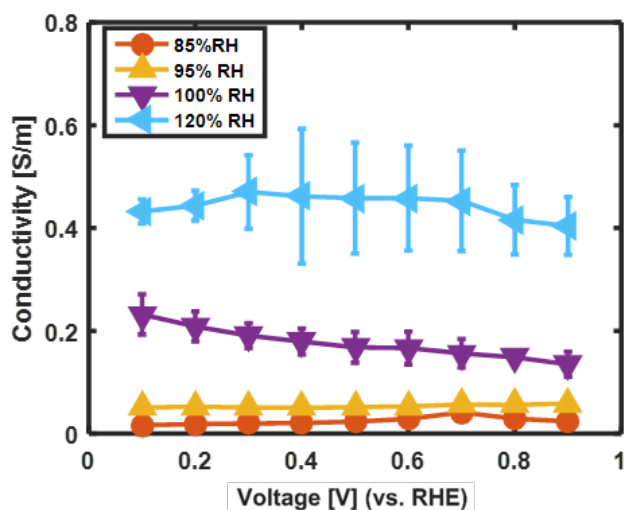


Figure 2.9: RH and potential dependence of ionic conductivity for Pt black ionomer-free electrode. The measurement was conducted at 85%, 95%, 100% and 120% RH respectively. Reprinted from [4], Copyright(2020), with permission from Wiley.

Considering observations above, we find that for a simple oxide-free metal surface (i.e., Au surface in the potential range studied here), the metal/water interface ionic conductivity can be modelled using classical EDL theory. However, such model can not describe the Pt surface. Some factors that may complicate the ion conduction on Pt surface are: (1) There are significant hydrogen adsorption at the Pt surface in the range below 0.4 vs. RHE and hydrogen gets removed from the Pt surface at higher potentials. In contrast, there is no hydrogen adsorption/desorption at the Au surface in the potential range we studied.

(2) At potentials above 0.75 vs. RHE, the Pt surface gets oxidized, which will introduce interfacial dipoles and later the surface charge [20]. The observed high conductivity in the low potential region (0.2 - 0.4 V), where the surface charge is expected to be small based on the classical EDL model, suggests that the high ionic conductivity is not due to increased proton concentration in this potential range. Our hypothesis is that at this low potentials, it is surface-adsorbed atomic hydrogen diffusion that is supporting the imposed current, probably by the forward and reverse Volmer reactions (Equation 2.6 and Equation 2.7).



where charge transfer reactions at the Pt/Nafion[®] interfaces convert the hydrogen between protons and adsorbed H atoms. The hydrogen adatoms can then diffuse across the electrode thickness. Although the rate of hydrogen surface diffusion on Pt in aqueous media is unclear, it is known to be sufficiently fast in vacuum [50]. Figure 2.10a illustrates this reaction-facilitated hydrogen transport mechanism. During the conductivity measurement with the MES, these reactions would occur at the interface between the Nafion[®] sensing layers and the electrode. In an ionomer-free cathode of a polymer electrolyte membrane fuel cell (PEMFC) MEA, the first reaction would occur at the Nafion[®]/Pt interface and the second reaction would occur at the position of the ORR. The electrons would be simultaneously conducted through the Pt to maintain charge neutrality. At potentials above 0.4 V, this mechanism would diminish due to the propensity for hydrogen to desorb as H⁺ as observed in CV measurements.

With this transport mechanism, one should be careful with the concept of conduc-

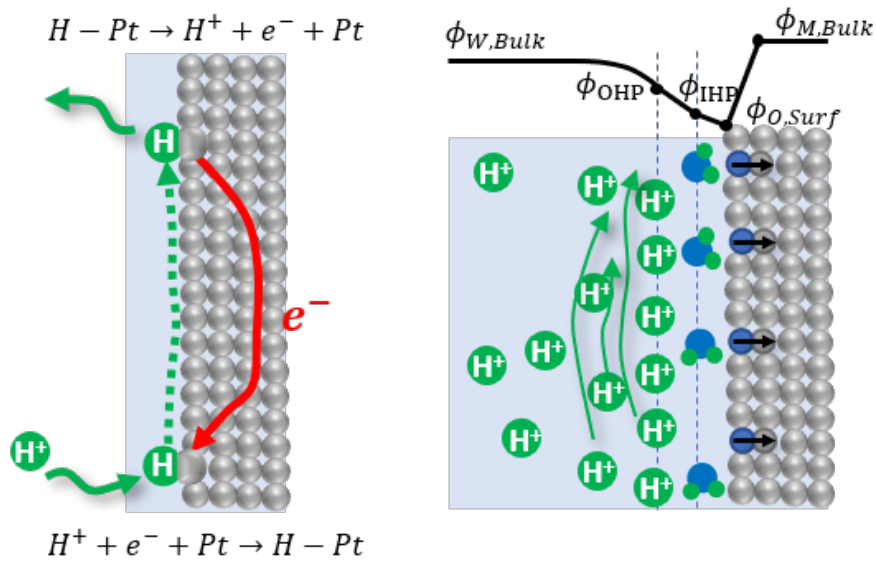


Figure 2.10: The reaction-facilitated adsorbed hydrogen diffusion transport mechanisms at low cathode potentials (left). The EDL charge transport of protons due to electromigration at moderate to high cathode potentials (right). Reprinted from [4], Copyright(2020), with permission from Wiley.

tivity since this is the diffusive transport of an uncharged species where the flux scales with surface concentration gradients. The observed potential difference during hydrogen pumping could be a manifestation of the small overpotentials associated with the forward and reverse Volmer reactions that would generate a finite potential difference in the water across the electrode since the overpotentials would be of opposite sign. The physics of this transport mechanism will be the subject of our future studies.

We postulate that the conductivity in the higher potential regions associated with EDL and oxide currents in the CV (i.e., above that of the H underpotential deposition current) is due to proton conduction in the water. Figure 2.10b illustrates this EDL charge transport of protons. We assume the water is acidic because the conductivity never goes through a minimum that would suggest a charge sign reversal. We also note that although possible effect of atmospheric carbon dioxide (CO_2) generating acidity in the water was not addressed, the measured conductivity is orders of magnitude higher than what one expects from the equilibrium formation of acid from atmospheric CO_2 . Thus, our results suggest the surface oxide dipoles are significantly altering the classical surface charge model, consistent with the non-monotonic surface charge model of Huang *et al.* [20]. It is also of note, that if a classical potential dependent surface charge was governing the conductivity through proton concentration in the water, we would observe contractions in the CV current where the conductivity is low. However, no contraction relative to an ionomer covered Pt black electrode is observed. One possible composition of different factors that contributes to the ionic conductivity at the Pt/water interface can be illustrated in 2.11. At low potentials, adsorbed hydrogen surface diffusion is contributing to the interface conductivity. At high potentials, electrical double layer and the surface oxide altered electrical double layer becomes dominant. More fundamental understanding of this mechanism may require detailed numerical studies. Thus, we suggest future modeling of proton transport on Pt surface consider both EDL proton electromigration considering oxide dipoles and

adsorbed H diffusion.

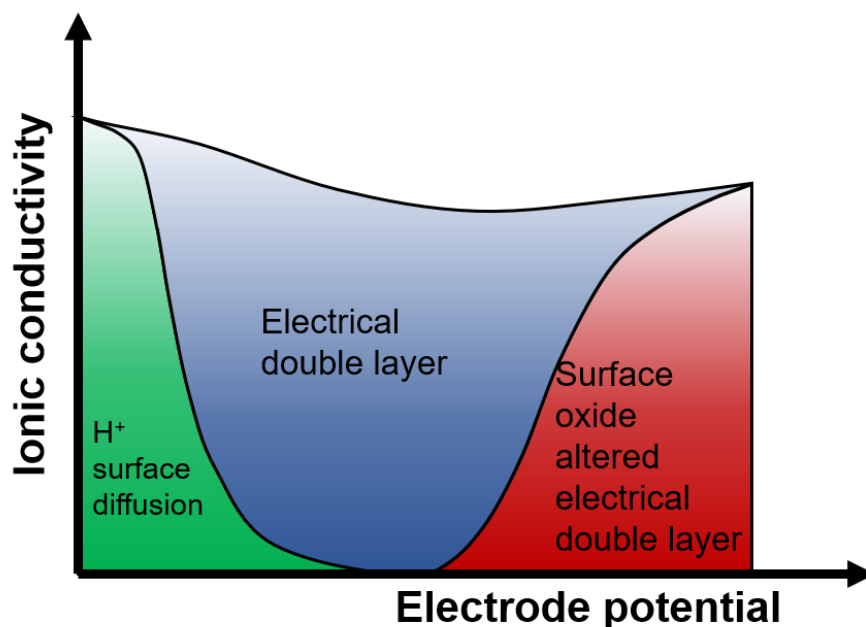


Figure 2.11: Illustration of different contribution to the Pt surface ionic conductivity at different electrode potentials.

2.4 Conclusions

In this chapter, we have investigated the ion transport and ORR reaction over extended metal surfaces in ionomer-free metal particle catalyst cathodes. Our primary focus was that of extended Pt surfaces, but we also studied the more ideal metal surface of Au. Au is an ideal reference surface because it lacks the H adsorption and oxide phenomena at relevant PEMFC ORR voltages. In addition, its significantly lower ORR activity relative to Pt in acidic conditions eliminated the intrusive effect of flooding in our analysis of water coverage. We found that the gold exhibited the expected correlation of the relative humidity dependence for the electrochemically active surface area and the ORR activity. It also exhibited the classical potential dependence for surface charge and conductivity,

with a minimum at the established PZC.

In contrast to Au, the Pt electrode showed substantially different behavior. The Pt showed the same scaling as Au for the relationship between ECRF and the ORR activity at currents where flooding was not problematic. The key difference between the Pt and Au results is the potential dependence of the conductivity. We put forth that these differences are an outcome of the more complex surface chemistry phenomena on the Pt surface at both low and high potentials; namely the H adsorption at low potentials and the oxide coverage at high potentials. The H adsorption provides a hydrogen transport mechanism at low potentials and the oxide coverage is presumed to keep the metal negatively charged at high potentials. These effects in concert with the conventional charge accumulation and conductivity in the EDL are hypothesized to be the origin of the relatively high and constant conductivity with Pt.

Chapter 3

Proton Transport at Carbon/Water Interfaces

3.1 Introduction

This chapter presents the study of the proton transport process at the carbon water interfaces. The polymer polymer electrolyte membrane fuel cell (PEMFC) is one of the most promising power generating systems for automotive applications due to its low tailpipe emission and high energy efficiency [6]. However, it is still not competitive with internal combustion engine vehicles because of its high cost [7]. For conventional PEMFCs using carbon supported Pt catalyst (Pt/C) catalyst, a large portion of their costs come from the platinum (Pt) [51], which cannot benefit from the economy of scale and might get higher as the demand of Pt increases. Though researchers have put a lot of efforts in bringing down the loading of Pt to below 0.1 mg/cm^2 on the anode and 0.4 mg/cm^2 on the cathode over the past decades [52, 15], the catalyst cost still serves as a major obstacle for PEMFCs' large market penetration. Further reduction of Pt loading is still required.

One effective way to further reduce the amount of Pt needed in the catalyst layer is by increasing the Pt utilization. The Pt/C based catalyst layer is a porous structure with

two major types of pores, i.e, the primary pores and the secondary pores. Primary pores are less than 10 nm in diameter and located inside carbon support particles. Secondary pores have larger diameters and are formed because of carbon particles' agglomeration. In between carbon particles, Nafion[®] ionomer serves as a binder and also provides a proton transport pathway, as shown in Figure 3.1. Park *et al.* [1] have examined different types of Pt/C catalysts using transmission electron microscope (TEM) and showed that a large portion of Pt particles is located in the primary pores of the carbon support. An ideal catalyst layer is that the Nafion[®] ionomer provides proton access for all available Pt surfaces. Unfortunately, in real applications, Nafion[®] mainly located at the exterior surface of the carbon support. Malek *et al.* [53] used coarse-grained molecular dynamics simulation and showed that ionomer can hardly penetrate through the primary pores of the carbon support. This ionomer distribution feature is also supported by experimental results [54]. It is believed that Pt inside the primary pores can be accessed by proton through condensed water, as shown in case 2 of Figure 3.1. Wang *et al.* [55] conducted numerical analysis and showed that water filled primary pores have strong proton transport capacity. Zenyuk *et al.* [56] used 2-pK surface complexation model and illustrated how carbon surface functional groups altered the carbon-water interface proton concentration. For Pt located at the exterior of the carbon support, water also plays an important role in facilitating the proton transport, as shown in case 3 of Figure 3.1. Soboleva *et al.* [57] conducted a parametric study on low ionomer loading catalyst layer and found that at high relative humidity (RH) conditions, water adsorbed on carbon surfaces compensates for low ionomer coverage in terms of proton conductivity.

In spite of water being important in facilitating proton transport in PEMFC catalyst layers, especially in ionomer poorly covered regions, there is no direct measurement of the property of this proton transport process. Iden *et al.* [23] used current interrupt and electrochemical impedance spectroscopy (EIS) to measure the proton conductivity of a pseudo

catalyst layer. Gazzarri *et al.* [24] used EIS to measure the cathode proton transport resistance. However, these previous works were conducted measuring the proton conductivity of the catalyst layer in whole, not the proton conductivity through water on carbon surfaces or carbon primary pores. Thompson *et al.* [22] investigated proton conduction on ionomer-free Pt surfaces, but not carbon surfaces. Paulus *et al.* [17] used glassy carbon to build model electrode and investigate the relation between Pt distribution and Pt utilization. However, the surface feature of glassy carbon is not representative of conventional carbon support used in fuel cell applications.

In this work, we investigated the proton conductivity of ionomer-free electrode based on Vulcan XC-72 and 10 wt% Pt/C. EIS and transmission line model were used to obtain the overall electrode proton conductivity. RH and electrode potential dependence study are also conducted.

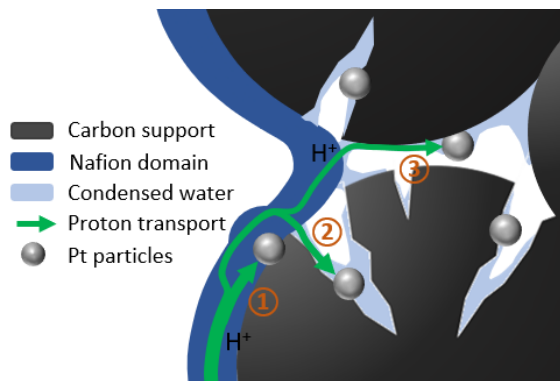


Figure 3.1: Schematic of proton transport inside catalyst layers at three different locations. 1: Pt particles covered with Nafion[®] ionomer. 2: Pt particles inside primary pores of the carbon support. 3: Pt particles in secondary pores of the carbon agglomerates.

3.2 Experimental

3.2.1 Sample preparation

Shown in Figure 3.2 is the schematic of the conductivity measurement sample. The anode is made of $6 \times 6 \text{ mm}^2$ gas diffusion electrode (GDE) (0.3 mg/cm^2 40% Pt on Vulcan carbon paper, Fuel Cells etc., College Station, USA). A proton exchange membrane (Nafion[®] 211, Ion Power, New Castle, USA) is placed in between the anode and cathode. For the cathode, a Kapton[®] film ($175 \text{ }\mu\text{m}$ thickness, McMaster-Carr, Aurora, USA) with a circular opening with a diameter of 3.2 mm was placed on to the membrane. Inside the circular opening, Vulcan carbon black (Vulcan XC-72R, Fuel Cells Etc, College Station, USA) or 10 wt% Pt/C (nominally 10% Pt on carbon, Alfa Aesar, Tewksbury, USA) was hand filled into the cavity as the ionomer-free electrode. On top of the ionomer-free electrode, a gas diffusion layer with a dimension of $6 \times 6 \text{ mm}^2$ was used (25BC, 5 wt% PTFE, Sigracet, Fuel Cells Etc, College Station, USA). The prepared sample was then assembled in the standard 5 cm^2 cell (Dual area fuel cell fixture, Scribner, North Carolina, USA). The cell temperature, as well as the anode and cathode gas flow rates and RHs are controlled by the fuel cell teststand (850e, Scribner, North Carolina, USA).

3.2.2 Impedance analysis

During the EIS measurement, the anode was supplied with hydrogen (hydrogen (H_2)) and the cathode was supplied with nitrogen (nitrogen (N_2)). The cell temperature was controlled to be 65°C . Both the anode and cathode gas flow rate were controlled to be 200 sccm. The AC impedance spectra were acquired using a commercial potentiostat (VSP, Bio-Logic, Claix, France). To study the potential dependence of the electrode conductivity, separate EIS measurements were conducted with ionomer-free cathode potential varied

from 0 V to 0.9 V in order to cover the fuel cell operating potentials. The sinus amplitude of the EIS measurement is set to be 1.0 mV with a frequency ranging from 1 MHz to 15 mHz. To study the RH dependence, impedance data were collected at three different RH conditions, i.e., 90%, 100%, and 120%. (It should be noted here that the 120% here means that the gas dew point temperature is above the cell temperature).

3.2.3 Cyclic voltammetry measurement

The cyclic voltammetry (CV) curves of Vulcan carbon and Pt/C ionomer-free electrode are measured using the same commercial potentiostat as that of EIS measurements. During the CV measurements, the cell temperature was controlled to be 65°C . The anode was supplied with 200 sccm H_2 , and the cathode was supplied with 200 sccm N_2 . The scan rate is 10 mV/s. For the Vulcan carbon electrode, a potential range of 0 to 1.0 V was used to avoid possible carbon corrosion reactions at potential higher than 1.0 V. For the Pt/C electrode, a potential range of 0 to 1.2 V was used, in order to capture the Pt-Pt oxide redox peaks at high potentials.

3.3 Result and discussion

3.3.1 Impedance response and transmission line model

As shown in Figure 3.3a is a simplified schematic of the conductivity testing cell. For the cathode side, in humid conditions, water will be adsorbed on the carbon surface. During EIS measurements, protons can transport through the water film, and ionomer-free carbon particles serve as the electric conducting media. Since the cathode is in an N_2 environment, there is no Faradaic charge transfer through the carbon/water interface, only electrical double layer capacitance will be formed at the carbon/water interface. The equivalent circuit

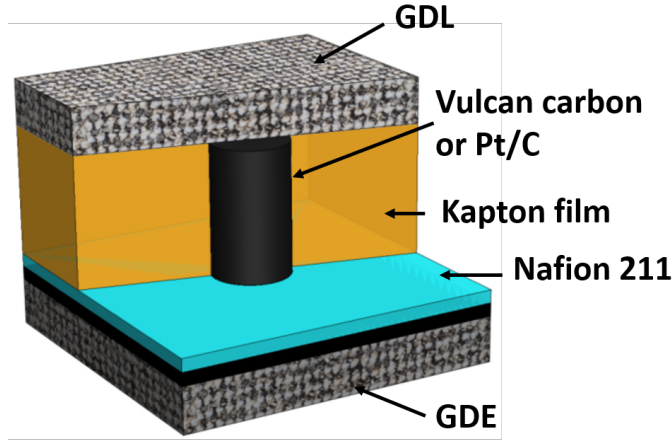


Figure 3.2: Schematic of the conductivity measurement sample. The upper part represents the cathode and the lower part represents the anode. A Nafion[®] 211 is used as the membrane. The cathode consists of Vulcan carbon black or 10 wt% Pt/C and GDL, and the anode is made of GDE

of the testing sample is shown in Figure 3.3b. This equivalent circuit is a simplification of that described in ref [58]. In the equivalent circuit, R_{proton} is the proton transport resistance, R_{carbon} is the electrical resistance of carbon porous material. Membrane resistance is shown as R_M , and C_{dl} is the electrical double layer capacitance.

Figure 3.3c is one typical impedance response of carbon ionomer-free electrode measured in H_2 (anode) and N_2 (cathode) environment at 120% RH, with carbon electrode potential held at 0.5 V. To get the proton transport resistance of the carbon electrode, two lines were fit according to the transmission line model. The first line was fit at the high-frequency region with a slop theoretically 45° relative to the real axis (shown in the figure as the first line). The intersection of the high-frequency line with the real axis indicates the membrane resistance. The second line was fit at the low-frequency region where the impedance plot curved up (shown in the figure as the second line). The projection of the segment of the first line to the real axis (shown in the figure as the distance between the

two dashed lines) will be one-third of the proton transport resistance of the carbon layer, $\frac{1}{3}R_{proton}$ [58, 22, 59].

Based on the proton transport resistance measured using the method mentioned above, the ionic conductivity of the porous electrode can be calculated as Equation 3.1:

$$\sigma_{ionic} = \frac{L_{electrode}}{\frac{1}{4}\pi D_{electrode}^2 R_{proton}} \quad (3.1)$$

where the $L_{electrode}$ is the length of the ionomer-free electrode, and $D_{electrode}$ is the diameter of the ionomer-free electrode.

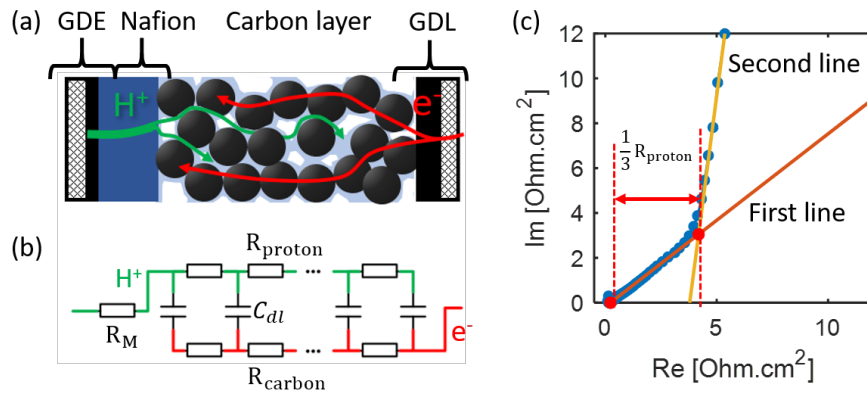


Figure 3.3: (a) Schematic of conductivity measurement setup. (b) The equivalent circuit based on the transmission line model. R_{proton} is the ionic resistance. R_{carbon} is the electrical resistance. R_M is the membrane resistance, and C_{dl} is the double layer capacitance. (c) Proton conductivity measurement based on the Nyquist plot.

3.3.2 Vulcan carbon electrode EIS results

Figure 3.4 shows the Nyquist plot of Vulcan carbon ionomer-free electrode at three different RH conditions. Figure 3.4a is the plots tested at 90% RH. At this RH condition, lines

at low-frequency region of the Nyquist plot doesn't show significant deviation from the high-frequency 45° line. To get the proton transport resistance, second lines at different potentials were fit based on the last 4 points in the low-frequency region. The proton transport resistance obtained from the EIS results shows a monotonic increase as the potential of the electrode increases, from 31.1 $\Omega.cm^2$ at 0 V to 712.6 $\Omega.cm^2$ at 0.7 V.

Figure 3.4b is the EIS results at 100% RH. A distinct transition of the Nyquist plot from high frequency region to low frequency region can be observed. As the RH increases from 90% to 100%, the proton transport resistance largely decreases. The R_{proton} is 118.8 $\Omega.cm^2$ at 0.7 V, one-sixth of that at 90% RH. Similar to Nyquist plots at 90% RH, the proton transport resistance increases monotonically as the electrode potential increases. It should be noted that the increase of proton transport resistance is small at the low potential range, as from 0 to 0.5 V, R_{proton} increases approximately 3 fold from 10.3 $\Omega.cm^2$ to 30.8 $\Omega.cm^2$. In contrast, as the electrode potential further increases from 0.6 to 0.8 V, the R_{proton} increases by 12 times. EIS measurement above electrode potential of 0.8 V was not conducted due to its high proton transport resistance.

Figure 3.4c shows the EIS results at 120% RH. Since the dew point of the gas is larger than the cell temperature, more water gets condensed inside the electrode than the 100% RH condition. The variation of R_{proton} with the electrode potential shows the same trend as that of 100% RH, for which the R_{proton} increases slowly from 5.0 $\Omega.cm^2$ at 0 V to 11.8 $\Omega.cm^2$ at 0.5 V and significantly increases from 17.9 $\Omega.cm^2$ at 0.7 V to 103.7 $\Omega.cm^2$ at 0.8 V. However, compared with 100% RH results, the proton transport resistance at 120% RH is smaller for each electrode potential.

3.3.3 Pt/C electrode EIS results

To examine whether the scattered Pt catalyst particles have some effect on the overall proton conductivity, a 10 wt% Pt/C catalyst was also tested using the same method, with re-

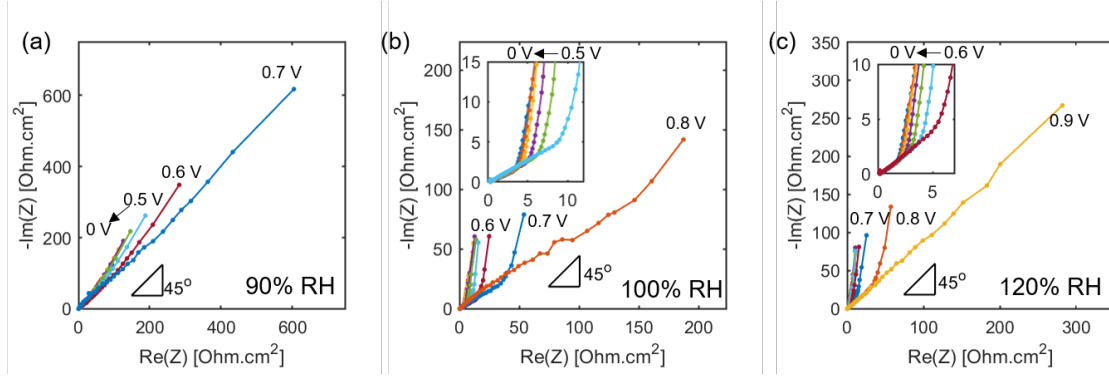


Figure 3.4: Nyquist plots of Vulcan carbon ionomer-free electrode at different RHs and electrode potentials. (a) 90% RH. (b) 100% RH (c) 120% RH.

sults shown in Figure 3.5. Since at 90% RH, the EIS results were not clear, measurements of Pt/C catalyst were only conducted at 100% and 120% RH. The electrode potential was controlled to be above 0.2 V to avoid the hydrogen evolution effect.

Figure 3.5a shows the EIS results measured at 100% RH. Compared with the R_{proton} of Vulcan carbon electrode at the same potential and the same RH condition, the R_{proton} of Pt/C ionomer-free electrode is much smaller, e.g., the proton transport resistance of the Pt/C electrode at 0.2 V is 5.2 $\Omega.cm^2$, while the value is 12.7 $\Omega.cm^2$ for the Vulcan carbon electrode. The difference in proton transfer resistance is likely caused by the difference in the carbon surface area of these two types of electrodes, which will be discussed in following sections. Similar to the Vulcan carbon electrode, the R_{proton} of Pt/C electrode shows similar dependence on the electrode potential. From 0.2 V to 0.5 V, the location where the Nyquist plot deviates from the 45° line slowly moves to the left in the plot, indicating higher proton transport resistance. As the electrode potential further increases from 0.6 V to 0.8 V, the increase in the R_{proton} becomes more significant. Shown in 3.5b is the EIS results at the 120% RH condition. The humidification condition also has a similar effect on the R_{proton} Pt/C electrode as that of the Vulcan carbon electrode. As the RH of the electrode increases from 100% to 120%, the R_{proton} decreases from 5.2 $\Omega.cm^2$ to 3.3

$\Omega.cm^2$ at 0.2 V and from 15.5 $\Omega.cm^2$ to 10.2 $\Omega.cm^2$ at 0.6 V.

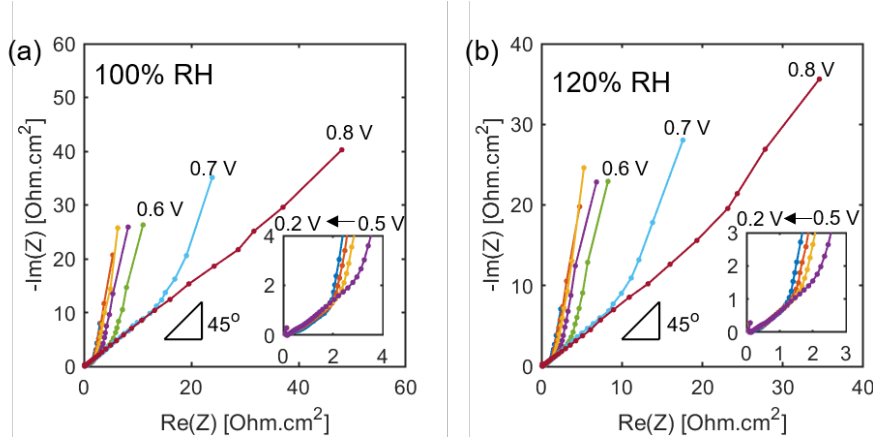


Figure 3.5: Nyquist plots of Pt/C ionomer-free electrode at different RHs and electrode potentials. (a) 100% RH. (b) 120% RH

3.3.4 Vulcan carbon and Pt/C electrode CV results

To provide more insight into the potential dependence feature of the proton conduction process on ionomer-free carbon and Pt/C electrode, CV measurements were conducted on the Vulcan carbon electrode and the Pt/C electrode, with results shown in Figure 3.6. For a CV test of Vulcan carbon in an electrolyte with good ionic conductivity [59, 60], the CV curve usually has a capacitor-like rectangular shape. The CV of ionomer-free Vulcan carbon electrode in Figure 3.6a, however, shows a strong dependence on the electrode potential. At potential region 0 to 0.6 V, the carbon electrode CV mainly shows the capacitive current in combination with two weak redox peaks located at around 0.1 V and 0.5 V, which could be related with carbon surface functional groups [60]. As the electrode potential increases to above 0.6 V, the currents for forward and backward scan start to decrease. The decrease of CV current at the high electrode potential corresponds well with the proton transport resistance's dependence on electrode potential. As the proton

conductivity of the porous electrode decreases, less carbon surface area is accessible to the proton, which leads to the decrease in capacitive current.

As the RH increases from 90% to 100%, there is an increase of the overall current for both forward and backward CV scans. The increase of CV current is likely caused by the capillary condensation in the mesopores and micropores of the electrode. Since water/carbon interfaces are the only medium for proton transport, the increase in carbon surface's water coverage results in larger accessible carbon surface area, thus a higher capacitive current. It should be noted that the increase of capacitive current from 90% to 100% RH corresponds well with the significant decrease of proton transport resistance of the Vulcan carbon electrode between these two RH conditions. Increase in the RH from 100% RH to 120% RH leads to a slight increase of CV current, indicating that the majority of the carbon surface has been covered with water. The further increase in water content as RH increases from 100% to 120% only leads to thicker water film and thus further decrease in proton transport resistance, as shown in EIS results.

Figure 3.6b is the CV of Pt/C at different RHs. At 0 to 0.2 V range, we can see peaks due to the hydrogen adsorption and desorption on Pt surfaces. However, at high potential range, Pt oxide formation and reduction peaks, which usually appears at a potential range of 0.6 to 0.8 V [61], are missing. The capacitive current due to the electrical double layer also decreases at high potentials. Both the absence of Pt oxide redox peaks and the decrease of capacitive current are suggesting a lower ionic conductivity in the catalyst layer and less accessible Pt and carbon surface area, which is consistent with the observation from EIS results. As the RH increases from 100% RH to 120% RH, a slight increase in the current density of the CV curve can be observed, indicating an increase of water content in the electrode.

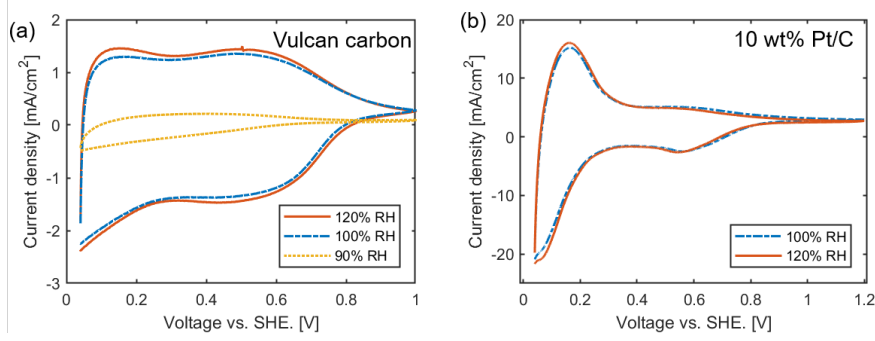


Figure 3.6: CV results at different RH conditions of (a) Vulcan carbon ionomer-free electrode, and (b) 10 wt% Pt/C ionomer-free electrode.

3.3.5 Proton conductivity comparison of the Vulcan carbon electrode and the Pt/C electrode

Based on the proton transport resistance obtained from EIS results, we can calculate the ionic conductivity of the electrode using Equation 3.1. As mentioned in section 3.3.2, the difference of proton conduction resistance between the Vulcan carbon electrode and the Pt/C electrode could come from the difference in the Vulcan and Pt/C loading. To compare the ionic conductivity between two electrodes, the calculated ionic conductivity of the Pt/C ionomer-free electrode was normalized by the double layer capacitance current density using Equation 3.2:

$$\sigma_{Pt/C.Normalized} = \sigma_{Pt/C.ionic} \frac{i_{Vulcan}}{i_{Pt/C}} \quad (3.2)$$

where $\sigma_{Pt/C.ionic}$ is the calculated Pt/C electrode conductivity, $\sigma_{Pt/C.Normalized}$ is the normalized Pt/C electrode ionic conductivity, i_{Vulcan} and $i_{Pt/C}$ are the double layer capacitance current density of the Vulcan carbon and the Pt/C electrode respectively. The

double layer capacitance current densities of two electrodes are calculated based on the average of the current density at 0.35 V of forward and backward CV scan at 120% RH. The calculated current density value was 1.45 mA/cm^2 and 3.67 mA/cm^2 for the Vulcan carbon electrode and the Pt/C electrode respectively.

The normalized ionic conductivity data is shown in Figure 3.7. The ionic conductivity values of the Vulcan carbon electrode are shown as dashed lines. At each RH, the ionic conductivity value decreases monotonically with the electrode potential. The maximum ionic conductivity for the Vulcan carbon electrode is 0.35 S/m at 0 V and 120% RH. It should be noted that, though this conductivity value is much smaller compared with a typical fuel cell catalyst layer with Nafion[®] as its ionomer, it is several orders of magnitude larger than pure water. The conductivity value decreases to 0.02 S/m at 0.8 V, more than an order of magnitude smaller compared with the maximum value at the same RH. The ionic conductivities of the Vulcan carbon electrode at 100% RH and 90% RH are about 50% and 80% less compared with that at 120% RH, respectively. The conductivity values at these RHs also show the same magnitude of decrease with increasing electrode potential as that at 120% RH.

The normalized ionic conductivity values of the Pt/C electrode are shown as solid lines. For 100% RH, ionic conductivity values of the Pt/C electrode are similar to that of the Vulcan carbon electrode. The conductivity values are slightly smaller of the Pt/C electrode at 120% RH compared with the Vulcan carbon electrode.

3.4 Conclusions

In this chapter, we have measured the ionic conductivity values of the Vulcan carbon ionomer-free electrode and the 10 wt% ionomer-free Pt/C electrode. In general, both electrodes' ionic conductivity is orders of magnitude larger than pure water. The dependence

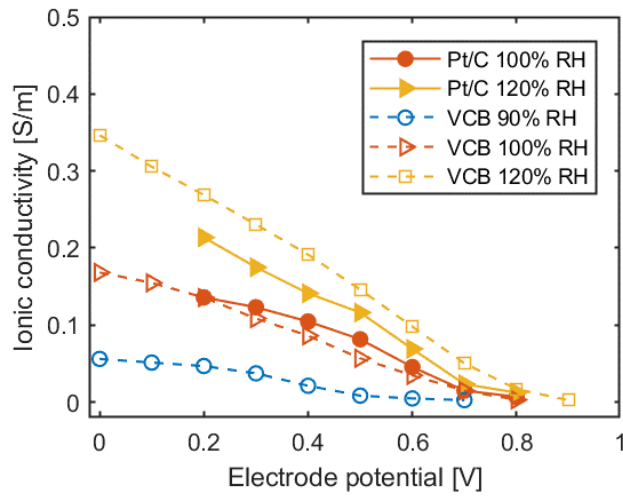


Figure 3.7: Comparison of the calculated ionic conductivity of the Vulcan carbon porous electrode and the Pt/C porous electrode at different RH conditions and different electrode potentials

of the ionic conductivity on the RH and the electrode potential are examined. The ionic conductivity of both electrodes shows a strong dependence on the RH. Results also show that within the fuel cell operating potential range (0 to 1.0 V), the ionic conductivity of the Vulcan carbon electrode decreases monotonically with the electrode potential. From the comparison of the ionic conductivity of these two electrodes, we found that the Pt catalyst on the carbon support has no significant effect on the overall ionic conductivity.

Chapter 4

Hydrogen Starvation at High Temperatures and Reversal Tolerant Catalyst Failure Mechanism

4.1 Introduction

This chapter will present the study on the failure mechanism of the reversal tolerant catalyst. Over the past decade, many efforts have been carried out to increase the durability of polymer electrolyte membrane fuel cell (PEMFC) during hydrogen starvation conditions. One popular strategy is the use of reversal tolerant anode (RTA) that incorporate oxygen evolution reaction (OER) catalysts, such as iridium oxide (IrO_2), to promote harmless water electrolysis over carbon corrosion and delay severe carbon support degradation. The present study investigates the RTA catalyst deactivation mechanism during hydrogen starvation conditions and the water activity dependence of the OER and carbon corrosion reaction to better understand the relatively quick failure of RTA at a high relative humidity (RH). The comparison of the OER durability under hydrogen starvation conditions of IrO_2 +carbon and IrO_2 alone membrane electrode assembly (MEA) shows that carbon deactivates the OER catalyst through carbon oxidation species poisoning. The catalytic

activity of IrO_2 and carbon oxidation rate are also separately measured in varying OER to investigate the water activity dependence of each reaction. The catalytic activity of IrO_2 measured by the current density response shows a linear dependence on OER, while the rate of carbon corrosion increases exponentially with RH. This linear versus exponential relationship suggests that the higher rate of catalyst poisoning at high OERs is related to the exponentially increased rate of carbon corrosion, resulting in the impaired durability of RTAs. The major part of the content in this chapter is in collaboration with Taigyu Joo, who conducted most of the experiments.

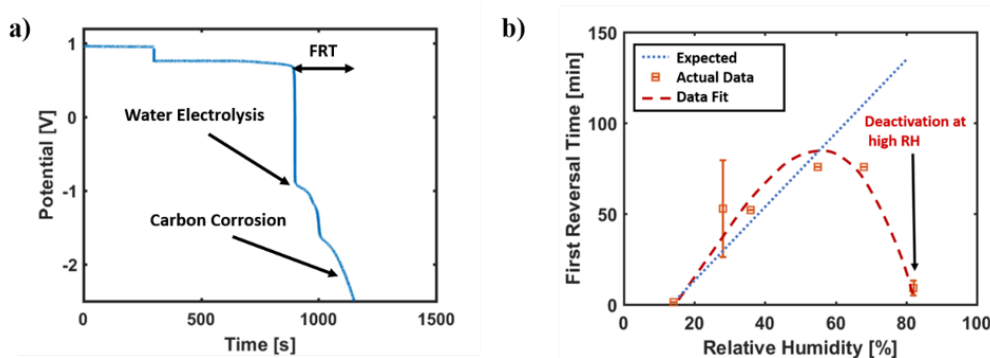


Figure 4.1: (a) Typical fuel cell voltage change with time during hydrogen starvation conditions. (b) Voltage reversal behavior of RTAs as a function of RH

4.2 Experimental

4.2.1 Sample preparation

To study the impact of carbon on catalyst deactivation, three different types of membrane electrode assemblies (MEAs) with active surface areas of 1 cm^2 were fabricated. All those three MEAs has an anode that consisted of IrO_2 synthesized by the Adams fusion method according to the literature [62, 63] using ionomer binder (Nafion[®] D521 grade, DuPont, USA). Each sample contained 5.0 mg/cm^2 of IrO_2 . For the first sample, no carbon black

was added to the anode (referred to as IrO₂ control sample). For the other two samples, an additional 1.0 mg/cm² of carbon black (Vulcan XC 72R, Fuel Cell Store, USA) was added to the anodes. The latter two samples were used to study the effect of carbon's presence on the anode (referred to as IrO₂ + C samples). The ionomer content in these three MEAs was fixed to 30 wt%. For the study of the effect of RH on deactivation, two additional 1 cm² MEAs were fabricated. One sample consisted of 5.0 mg/cm² of IrO₂ catalyst (IrO₂ 99.9% trace metals basis, Sigma-Aldrich, USA) (referred to as IrO₂-only sample), while the other sample consisted of 1.0 mg/cm² of carbon black (Vulcan XC 72R, Fuel Cell Store, USA) (referred to as carbon-only sample). For these two samples, the ionomer was fixed at 1:1 volume ratio between the ionomer and IrO₂ or carbon, depending on the material used on the anode.

In assembling the MEA, a perfluorinated sulfonic acid ionomer membrane (Nafion[®] NRE 115, DuPont, USA) was used to separate the anode and cathode. polytetrafluoroethylene (PTFE) (McMaster-Carr, USA) sub-gaskets of 432 and 156 μ m thick were used on anode and cathode side, respectively to maintain the gas diffusion layer (GDL) compression at or below 80%. Gold-sputtered titanium (Ti) mesh was used on the anode side as a carbon-free GDL. On the cathode side, a commercial gas diffusion electrode (GDE) (0.3 mg/cm² Pt, Fuel Cell Store, Texas, USA) was used for all MEAs.

4.2.2 Study protocol

The fabricated MEAs were assembled into specially designed fuel cell hardware. To remove all sources of carbon on the anode side, the graphite flow plate was replaced with corrosion resistant Ti mesh and Ti current collector. A commercial fuel cell test stand (850 Test stand, Scribner Associates Inc., North Carolina, USA) was used to control the gas flow rate and RH. A potentiostat (VSP, Bio-Logic, Claix, France) was used for all electrochemical measurements. For the IrO₂-only sample in the RH dependence study, a Pt

sputtered Ti mesh was used on the anode side as a GDL. For the carbon-only sample, a gold sputtered Ti mesh was used. The gold sputtering was used to reduce OER current obtained with a Pt coating relative to the low carbon OER current. In the case of the IrO₂ sample, the Pt-coated Ti mesh contributes a negligible amount of OER current (orders of two difference) relative to the OER current produced by the IrO₂ catalyst particles because the Pt active surface area is smaller.

For experiments studying the effect of carbon in deactivating IrO₂ catalyst, the cell was held at 65°C. For the RH dependence studies, the cell was controlled at 90°C to provide a broader range of RH conditions. To simulate hydrogen starvation conditions, nitrogen gas at 100% RH was supplied to the anode with a flow rate of 0.4 L/min, while 100% RH hydrogen was supplied to the cathode with a flow rate of 0.134 L/min. A current density of 1 A/cm² was applied to mimic the cell reversal in a typical hydrogen starvation condition with a cut off potential of 6 V. The voltage response was recorded in five repeated experiments in our study on the effect of carbon on the RTA catalyst.

Before and after each simulated hydrogen starvation experiment on the effect of the presence of carbon, we conducted cyclic voltammetry (CV) measurements on the anode to examine the electrode damage due to cell reversal (i.e. hydrogen starvation). For the CV measurement, the cell temperature was maintained at 65°C. The anode was supplied with nitrogen at 0.4 L/min, and the cathode was supplied with hydrogen at 0.134 L/min both at 100% RH. The CV scans were conducted from 0.04 to 1.2 V with a scan rate of 25 mV/s. The MEAs were imaged by scanning electron microscope (SEM) (XL-30 FEG SEM, Philips, USA) to observe the structural changes caused by cell reversals.

For our studies on the RH effect with the IrO₂-only sample, potentials of 1.6, 1.7, and 1.8 V were held for two minutes each under varying gas RH. Those potentials were selected because they are typical of the anode voltage during cell reversal when the majority of the current is from OER. Thus, we are exploring the deactivation processes while the

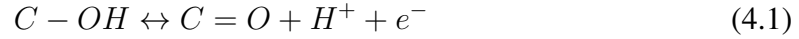
cell is still in the OER regime. The current density responses were recorded at each RH and potential using the potentiostat until three consecutive current response sets showed stable responses. In case of the carbon-only sample, the same potentials were applied for 15 seconds and repeated for six times under each RH condition. The short duration of potential hold is to prevent severe electrode damage. The last three current response sets were averaged for both samples to compare the electrochemical reaction rates of OER and carbon corrosion reaction.

4.3 Results and Discussion

4.3.1 Effect of carbon

Figure 4.2a shows the comparison of the anode half-cell potential of the two samples. The red dashed line shows the anode half-cell potential of the IrO_2 control sample, while the solid lines show five successive reversal tests for the IrO_2+C sample. The IrO_2 control sample maintained OER with its anode half-cell potential constant at 2.2 V for over 20 hours. In contrast, the anode half-cell potential of the IrO_2+C sample increased to the 6 V cutoff voltage in about 20 seconds, meaning the sample could not support the current density through Faradaic OER or carbon corrosion reaction current. The initial anode potential for OER was similar to that of the IrO_2 control, but the potential increased rapidly after approximately 20 seconds, which is similar to the cell voltage response in the previous study with PEMFCs[14]. Moreover, the successive hydrogen starvation tests all resulted in rapidly increasing voltage with the reversal times being shorter than that of the first test, where the majority of the carbon corrosion would have occurred. The observation of stable OER current with just IrO_2 and rapid failure with minor amounts of carbon indicates that the presence of carbon causes the deactivation of IrO_2 .

Figure 4.2b shows the CV measurements of the IrO₂+C sample. The CV curves were measured below the standard potential of water electrolysis before and after each reversal test to further understand the effect of the carbon to the IrO₂ catalyst. The black dashed line in Figure 4.2b shows the CV measurement for the beginning of life (BOL) IrO₂+C sample. The BOL CV curve shows significant peaks attributed to IrO₂ at about 0.75 V [64]. After the first reversal, new peaks near 0.6 V appear. These peaks are attributed to the hydroquinone-quinone (HQ-Q) redox reaction from the surface oxidation of the carbon [65, 60]:



These HQ-Q peaks decrease in height as the sample undergoes consecutive reversal tests, indicating that the carbon is getting oxidized and corroded. The reduction in height can be attributed to additional loss of carbon and HQ-Q sites with additional reversals.

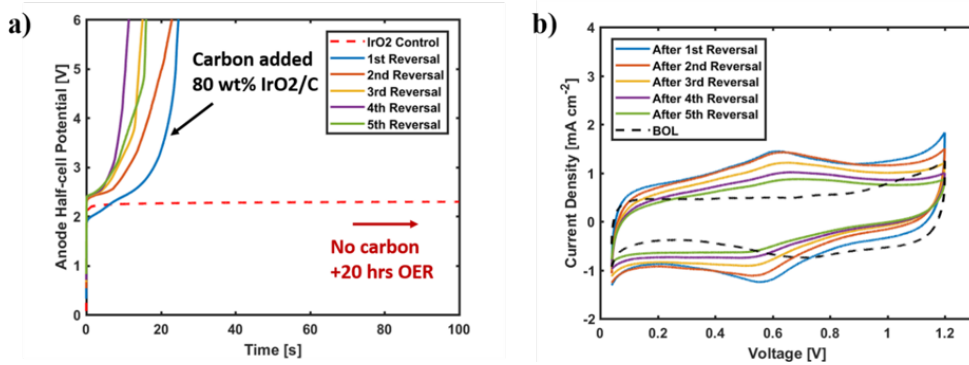


Figure 4.2: (a) Anode potential change during OER of IrO₂ control and IrO₂+C samples operated at 1 A/cm². (b) CV curves of the IrO₂+C sample before and after each reversal test.

Sections of the tested MEAs were imaged by SEM to analyze the corrosion and change in electrode structure. Figure 4.3a shows the anode surface of the pristine IrO₂+C sample

used (i.e. BOL). The bright white particles are the agglomerates of IrO_2 that are surrounded by the carbon black and bound by Nafion[®] ionomer. In contrast, Figure 4.3b shows the anode surface of the IrO_2+C sample after the reversal test. The end of life (EOL) image indicates the presence of similar particles, but the surface is corroded compared to that of the BOL image. This result agrees with the decreasing HQ-Q redox peaks in Figure 4.2b, which suggests that the carbon is getting oxidized and corroded. For comparison, the EOL image of IrO_2 control sample is shown in Figure 4.3c. In contrast to the BOL and EOL images of the IrO_2+C sample, the image shows agglomerated IrO_2 particles and no obvious sign of IrO_2 loss. This difference in morphology further supports that IrO_2 does not get deactivated by itself during OER, but rather the deactivation is triggered when carbon is present.

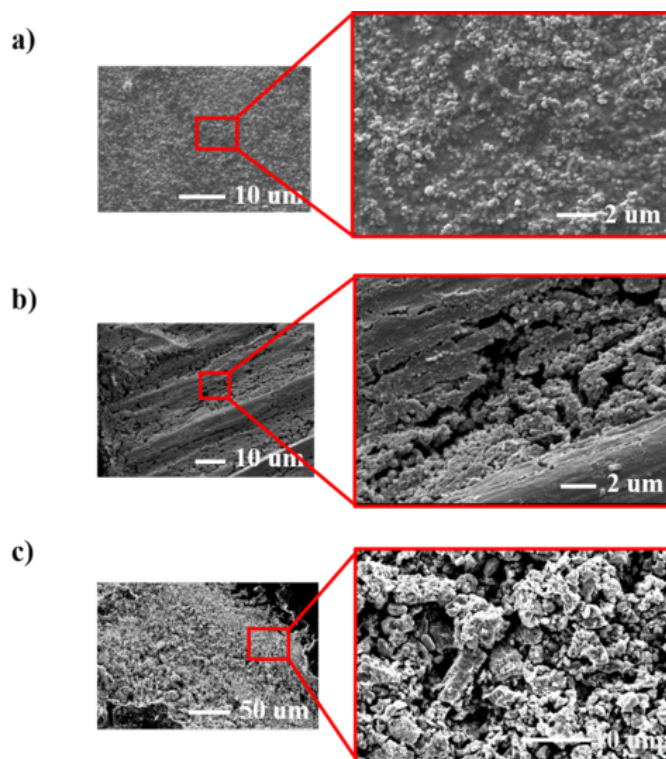


Figure 4.3: SEM images of anode surfaces from (a) BOL IrO_2+C sample, (b) EOL IrO_2+C sample, and (c) EOL IrO_2 control sample that has undergone cell reversal at 100% rh

4.3.2 Deactivation mechanism

The effect of carbon on deactivating the IrO₂ OER was confirmed in the previous section. However, the deactivation mechanism was not resolved. Figure 4.4 shows the two possible ways that the addition of carbon may have deactivated the IrO₂ following simulated reversal experiments. The first mechanism, shown in Figure 4.4a, is the loss of electronic connectivity of the catalyst due to the loss of the carbon between the IrO₂ particles. When a significant amount of carbon black is mixed with IrO₂, a minor amount of thermodynamically feasible carbon corrosion could occur at the typical OER voltages. This minor amount of carbon loss may cause the IrO₂ to be electrically isolated and thus a “physical deactivation”. The second mechanism illustrated in Figure 4.4b is a chemical deactivation of the OER catalyst caused by species generated from the carbon oxidation reaction at OER voltages. As the carbon oxidizes, it may poison the OER catalyst surface so that the latter no longer acts as an active OER catalyst [66].

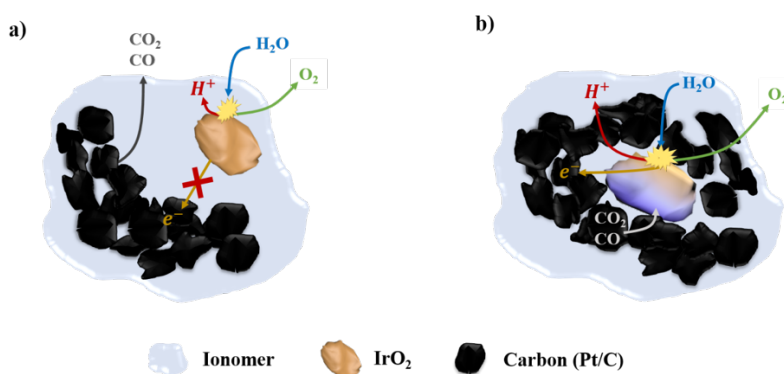


Figure 4.4: A schematic illustration of the two possible RTA failure mechanisms: (a) loss of electronic connectivity to the OER catalysts due to degradation of the carbon support and (b) poisoning of the OER catalyst by species generated during carbon oxidation reaction.

To investigate which mechanism deactivates the OER catalyst, a sample with distinct

layers was tested with the same experimental protocol. As shown in Figure 4.5a, the carbon and IrO₂ catalyst were separated into two different layers. This configuration allowed the OER catalyst to maintain direct contact with the current collector independent from the carbon layer; thus, the electrical connectivity was maintained even if the carbon layer below was fully oxidized. Figure 4.5b shows a comparison of the anode potential of the stratified sample and the control IrO₂ under reversal conditions. The red dashed line shows the anode potential of the IrO₂ control sample, which maintains its anode potential at 2.2 V. In contrast, the anode potential of the layered sample quickly increased to the cutoff voltage of 6 V in about 20-25 seconds. Figure 4.5c shows the CV responses of the layered sample before and after each reversal test below the standard potential of water electrolysis. The BOL CV measurement, shown in the black dashed line, shows a similar response to that of Figure 4.2b. After the first reversal, the HQ-Q redox peaks appear near 0.6 V and decrease as successive reversals experiments were performed, indicating the corrosion of the carbon layer. This failure with carbon is similar to the previous experimental results with the mixed carbon and IrO₂ and indicates that the OER catalyst was deactivated even when the electrical connectivity was maintained with the current collector. Thus, the deactivation mechanism of OER catalyst is likely to be chemical deactivation via the poisoning by carbon oxidation species, rather than losing electrical connectivity.

4.3.3 Water activity dependence study

To understand the mechanism behind the increased deactivation rate of IrO₂ at high RHs, we evaluated the RH dependence of the IrO₂ OER and the carbon oxidation reaction separately. Potentials of 1.6, 1.7, and 1.8 V were then applied to the MEAs with nitrogen at various RH conditions to obtain the approximate reaction rates during reversal conditions.

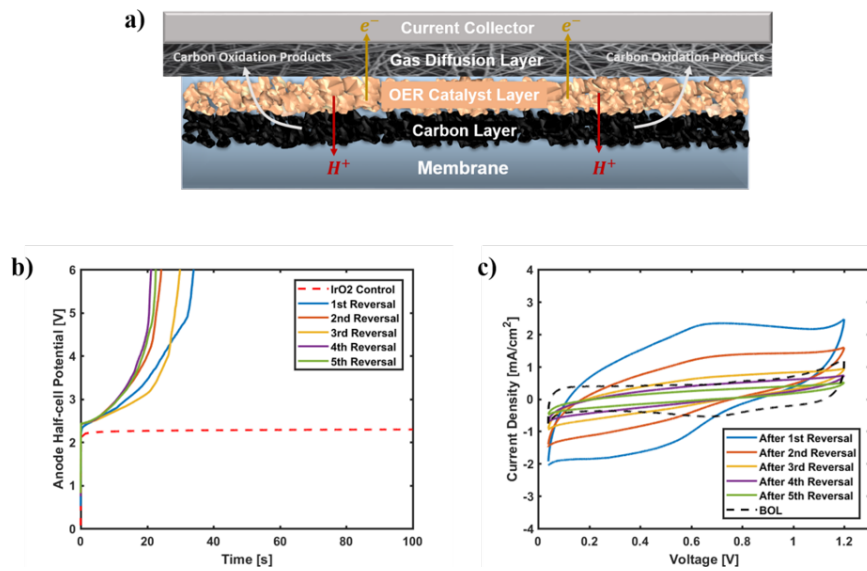


Figure 4.5: (a) Schematic of the layered sample for studying the effect of electrical connectivity on IrO_2 deactivation. (b) Comparison of anode half-cell potential during OER in IrO_2 and stratified IrO_2+C sample operated at $1 A/cm^2$. (c) Comparison of CV before and after each reversal test of the layered IrO_2+C sample.

Current density is directly proportional to the reaction rate by the following equation [60]:

$$\text{Reaction rate (mol/s)} = \frac{j \cdot A}{n_{e,i} \cdot F} \quad (4.2)$$

where j is the current density, A is the electrode area, $n_{e,i}$ is the number of electrons transferred per substance, and F is the Faraday's constant. The averages of the last three consecutive current density responses are plotted in Figure 4.6a and 4.6b for the IrO_2 and carbon samples, respectively. As shown in Figure 6a, the catalytic activity of IrO_2 shows a linear dependence on RH. The significant increase in current at higher voltage indicates that the cell was not mass transport or ohmic limited.

In contrast to the linear response by the IrO_2 OER catalyst, the rate of the carbon corrosion reaction for the carbon-only sample shown in Figure 4.6b increased exponentially with RH. Note that the current density due to carbon oxidation reaction is two orders of magnitude lower than the IrO_2 OER current density. That is because we are evaluating the RH dependence at the voltages of the OER dominated current during reversal, which is prior to the subsequent anode voltage increase when the IrO_2 deactivates, and the carbon corrosion reaction becomes dominant.

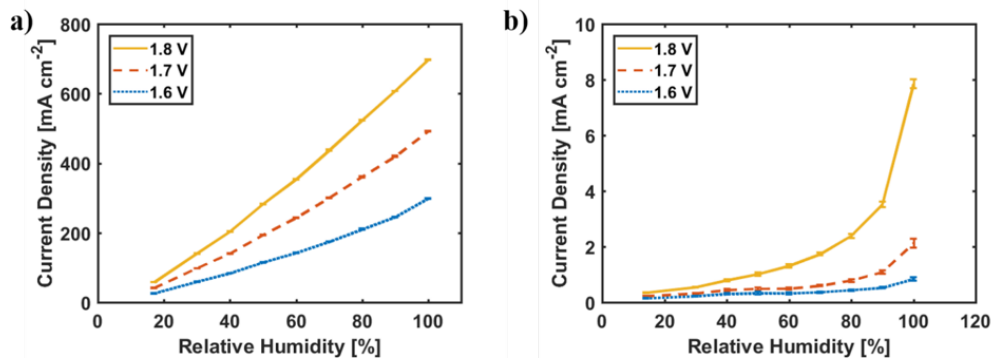


Figure 4.6: Current density response of (a) OER with an IrO_2 -only sample and (b) carbon oxidation with a carbon-only sample at various rhrs based on potential holds at 1.6, 1.7, and 1.8 V.

The exponential increase of the carbon corrosion reaction with RH indicates that there is a higher rate of carbon oxidation species being produced at higher RH. If these species are responsible for the chemical deactivation, then the rate of deactivation would increase at higher RH as illustrated in Figure 4.7. The carbon corrosion current increases most dramatically above 80% RH, which is also where we observe the decrease in first reversal time (FRT) from our previous reversal studies conducted on PEMFC anodes, as shown in Figure 4.1. To summarize, the RH dependence comparison shows that the decreased FRT of RTAs at high RHs can be attributed to the increase in the rate of the minor carbon oxidation current at these OER voltages. Also, these results show that even though OER is dominant in RTAs when in the water electrolysis voltage plateau during the reversal, there is thermodynamically favorable carbon corrosion that leads to RTA failure.

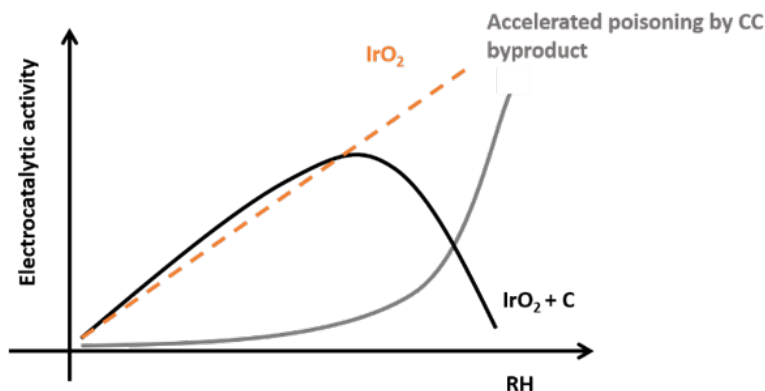


Figure 4.7: A schematic showing the behavior of RTA electrocatalytic activity and the acceleration of the poisoning rate caused by the carbon oxidation reaction byproduct as rh increases.

4.4 Conclusions

In this chapter, we have conducted cell reversal experiments to evaluate the failure mechanism of RTAs and increased rate of failure at high RH. Reversal experiments provide evidence that the OER catalysts are deactivated by species generated during carbon corrosion rather than electrical isolation due to the loss of carbon support. The water activity study found that the OER of IrO_2 increases linearly with RH, while the rate of carbon oxidation reaction increases exponentially with RH. Combining these two results suggests that the performance of RTAs drop significantly at high RH due to accelerated poisoning by carbon corrosion byproducts at high RH.

Chapter 5

Investigation of Hydrogen Starvation in Subfreezing Conditions

5.1 Introduction

This chapter will present the study on cell reversal in freezing conditions and damage mitigation strategies. Automotive fuel cells can suffer from cell voltage reversals due to hydrogen fuel starvation at the anode, which can be exacerbated by subfreezing temperatures because of extensive ice formation and its blockage of the hydrogen supply channels. Here we report on low temperature (-15 to 45°C) reversal degradation due to hydrogen starvation and evaluate the use of a reversal tolerant anode (RTA) with an oxygen evolution reaction (OER) catalyst (e.g., iridium oxide (IrO_2)). During subfreezing cell reversal, we observed a water electrolysis cell voltage plateau, but the typically subsequent voltage plateau for carbon corrosion usually seen at high temperatures was not found. Repeated cell reversal tests at subfreezing temperature shows a much slower degradation rate compared with high temperature reversals. A series of isothermal reversal tests at different temperatures indicate that the degradation rate related with carbon corrosion is temperature dependent. As for the effect of RTA on the cell reversal behavior, we found at sub-

freezing temperatures that the voltage reversal duration time of the membrane electrode assembly (MEA) with RTA is similar to that of the MEA without RTA. However, once the cell temperature was sufficiently above freezing, such as during the heating of the startup process, the MEA with RTA would facilitate water electrolysis reactions by consuming water and delaying the onset of carbon corrosion. Thus, our results show that cell reversal with subfreezing internal temperatures does not substantially degrade the anode by carbon corrosion, but that as the cell warms an RTA is one approach to extend the survival of the fuel cell stack. Part of the results were published in paper [3].

5.2 Experimental

5.2.1 MEA and fuel cell fabrication

An in-house MEA with an active area of 4 cm^2 was fabricated using a perfluorosulfonic acid (PFSA) membrane (Nafion[®] NRE200CS (H⁺) form, DuPont, USA) and electrodes consisting of carbon supported Pt catalyst (Pt/C) catalyst (HISPEC4000[®] grade, Johnson Matthey, UK) and an ionomer binder (Nafion[®] D2021 grade, DuPont, USA). The anode and cathode Pt loadings were 0.1 and 0.4 mg_{Pt}/cm², respectively. The ionomer binder content in the electrode was 30 wt% with respect to the total solid content of the dried electrode. For preparing the RTA, an acid-stable water electrolysis catalyst, IrO₂, was synthesized using the Adams fusion method [62, 63]. To compare the effectiveness of IrO₂ during cell reversal in freezing conditions, two types of MEAs were fabricated, one with no IrO₂ in the anode (i.e., 0 wt% RTA MEA) and the other one with 5 wt% IrO₂ in the anode with respect to the amount of Pt catalyst in the anode (i.e., 5 wt% RTA MEA). Adhesive-backed polyimide Kapton[®] (25 μm thickness, McMaster-Carr, Aurora, USA) films were used as subgaskets. We assembled the MEAs in commercial fuel cell test-

ing hardware (Dual-area fuel cell fixture, Scribner Associates Inc., North Carolina, USA) with commercial gas diffusion layer (GDL)s (25BC grade, SGL Technologies, GmbH, Germany). A commercial fuel cell test station (850 Test stand, Scribner Associates Inc., North Carolina, USA) was used to record the gas conditions and the anode and cathode potentials. The cell potential during reversal testing was recorded using a potentiostat (VSP, Bio-Logic, Claix, France).

5.2.2 Reference electrode

During hydrogen-air cell experiments, a hydrogen reference electrode was used to monitor the cathode and anode potential change [67]. Figure 5.1a shows a schematic of the cross-section of the reference electrode. We used a strip of the polymer electrolyte membrane (Nafion[®] 211 grade, IonPower, New Castle, USA) as the electrolyte bridge. A polyimide Kapton[®] film was used as a covering to prevent any loss of water from the Nafion[®] strip. One end of the Nafion[®] strip was in contact with a 1 cm² gas diffusion electrode (GDE) (0.3 mg_{Pt}/cm², 40 wt% Pt on Vulcan, carbon paper, Fuel Cells Etc., College Station, USA) inside a custom-made acrylic hardware that provided gas sealing and good contact between the GDE and the Nafion[®] strip as well as connected the reference electrode to the fuel cell hardware. A Pt sputtered stainless steel plate was used to further ensure good electrical contact with the GDE of the reference electrode. The other end of the Nafion[®] strip was in contact with an overhanging edge of the PFSA membrane in the MEA. Figure 5.1b shows a top view of the integration of the reference electrode with the MEA that was subsequently inserted into the fuel cell hardware. As we previously described [68], an electrode misalignment between the anode and the cathode with an overhang distance of δ was intentionally introduced (as shown in Figure 5.1a). Adler *et al.* [69] reported that if the ratio of the electrode misalignment divided by the membrane thickness d (i.e., δ/d) is greater than 4, then the reference electrode (RE) would measure the ionic potential

at the interface between the overhanging electrode and the membrane. The δ and the membrane thickness d values were fixed to be 1 mm and 25 μm , respectively, resulting in the δ/d ratio value of 40 which is greatly larger than 4. Thus, our reference electrode is primarily isolating the potential of the anode in these measurements. It should be noted that the reference electrode measured the electrolyte potential on the anode side near the overhanging part, which can differ from the anode potential in other regions, particularly during gas switching. However, as shown in our previous work [68], the measurement error is acceptable in terms of monitoring the anode potential change when the overall cell voltage change is highly complex due to several simultaneous processes in the hydrogen-air freezing reversal tests, as will be shown later.

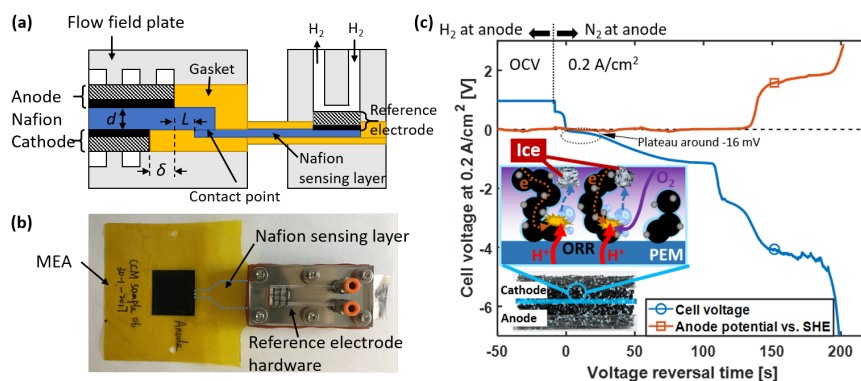


Figure 5.1: (a) Cross-sectional schematic of the reference electrode and its connection with the MEA. (b) A top view image of the reference electrode hardware and its integration with the MEA. The dashed lines represent the Nafion[®] sensing layer in between the [®] subgaskets. (c) Cell and anode potential changes of 0 wt% RTA MEA during hydrogen-air cell reversal tests as a function of time at a subfreezing temperature of -15°C. Reprinted with permission from [3], Copyright(2020), American Chemical Society.

5.2.3 Hydrogen starvation and cell reversal testing protocol

Hydrogen-air cell reversal experiment

We performed these tests to investigate the simultaneous effects at the cathode and anode during reversal at subfreezing conditions when the cathode is generating water. We initially operated the cell at a constant current density of 0.2 A/cm^2 with anode and cathode supplied with hydrogen (flow rate: 134 ml/min) and air (flow rate: ml/min), respectively. Then the anode hydrogen supply was manually switched to nitrogen with the same flow rate. Both the anode and cathode potential changes were monitored using the reference electrode. We controlled cell at below room temperature using an environmental chamber (Model TJR, Lunaire Limited, USA). During reversal tests at temperatures below room temperature (i.e., 25°C), both the anode and the cathode gases passed through humidifier water tanks at 25°C before being supplied to the cell. For cell temperatures above room temperature, we set humidifier temperatures to be the same as the cell temperature so the relative humidity (RH) of the gases was 100%. The reference electrode was used for the hydrogen-air cell reversal tests. Hydrogen was supplied to the reference electrode hardware with a flow rate of 100 ml/min. The reference electrode's electrolyte was pre-humidified at 65°C and 100% RH before insertion into the environmental chamber.

Hydrogen-pumping cell reversal experiment

We designed our hydrogen-pumping experiments to specifically focus on the anode and isolate it from the freezing degradation at the cathode. We initially supplied the anode with hydrogen (flow rate: 134 ml/min) but the cathode was fed with nitrogen (flow rate: 428 ml/min) instead of air, resulting in a hydrogen evolution reaction (HER), i.e., $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, at the cathode, which renders its potential close to zero allowing for its use as a reference point during freezing reversal tests. We also operated at a constant

current density of 0.2 A/cm^2 during these tests and the temperature and RH control were the same as the hydrogen-air cell reversal experiments.

5.2.4 Electrochemical characterization

After the cell reversal experiment, we characterized the cell at a normal temperature of 65°C . The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and polarization curve measurements were conducted to examine the electrode damage due to hydrogen starvation and cell reversal. For the cathode CV and EIS measurements, the cell temperature was 65°C and the gases were delivered at 100% RH. In both measurements, we supplied the anode with hydrogen at a flow rate of 134 ml/min . During CV, we supplied the cathode with nitrogen at a flow rate of 134 ml/min . The CV scan was conducted from 0.04 to 1.2 V at a scan rate of 50 mV/s . During EIS, we fed the cathode with air at 428 ml/min . The EIS spectra were measured at 0.1 and 0.4 A/cm^2 . For the polarization curve measurements, the temperature and gas conditions were the same as those of EIS. The cell voltage was recorded at constant current densities ranging from 0.0 to 1.6 A/cm^2 .

5.2.5 Characterization by SEM and EDS

Cross-sectional specimens of MEAs were obtained by fracturing in liquid nitrogen. The cross-sectional morphology of anodes was analyzed using an scanning electron microscope (SEM) (Quanta 600 FEG, FEI Company, OR, USA) with its secondary electron detector and energy dispersive spectroscopy (EDS) (Noran Vantage DSI, Thermo Noran, WI, USA) detector. The GDL was carefully separated from the anode catalyst layer using tweezers to image the anodes top surface.

5.3 Results and discussion

5.3.1 Hydrogen-air cell reversal experiment

Figure 5.1c shows the cell and anode potential changes during hydrogen-air cell reversal tests as a function of time at a subfreezing temperature of -15°C . The voltage reversal time shown on the x-axis was the duration of time cell's voltage stayed negative. The open circuit voltage (OCV) of the cell was recorded before the reversal test under normal supply conditions of hydrogen and air to the anode and the cathode, respectively. The OCV was 0.96 V while the anode potential was around 0 V. Then, a constant current density of 0.2 A/cm^2 was applied to the cell with the hydrogen fed being simultaneously replaced by nitrogen, in order to simulate cell voltage reversal conditions. At 0.2 A/cm^2 , the cell voltage quickly dropped to a small negative value of -16 mV, for a short plateau of roughly 30 s. We surprisingly observed that during the freezing reversal at -15°C for about 130 s, the cell voltage of the 0 wt% RTA MEA decreased relatively gradually down to about -3 V, but the anode potential did not increase significantly and remained stable, indicating there was still hydrogen present from the slow displacement of hydrogen from the test stand. Thus, the observed decrease in cell voltage during freezing reversal tests for the first 130 s of reversal duration time is primarily a result of a decrease in the cathode potential. This unstable cathode potential was also observed in prior cold-start studies[70, 71, 72]. The oxygen reduction reaction (ORR) at the cathode continuously generates water, and thus in freezing conditions, ice is formed inside the cathode and blocks the pores essential for oxygen transport. Local depletion of oxygen with applied currents leads to the HER instead of the ORR at the cathode, which is attributed to the short plateau formation of cell voltage at around -16 mV. As the ice kept forming and filling more pores in the cathode, the overpotential for the ORR increased and the cell potential slowly decreased to and

plateaued at around -1 - -1.2 V, which was followed by a relatively rapid drop down to -3 V without causing any significant increase in the anode potential, suggesting an effect isolated to the cathode.

After 130 s of cell reversal time, the cell presented a significant increase of anode voltage and then a plateau at 1.6 - 1.8 V that is consistent with water electrolysis reaction. During this time, the cell voltage is a very negative value of -4 V. After 60 s duration of the water electrolysis plateau at the anode, the anode potential sharply increases, and cell voltage drops to -7 V at the termination of the experiment. This anode behavior is in clear contrast to previous observations at higher temperatures, e.g., 60 - 90%, where the cell voltage dropped and the anode potential increased quickly during reversal tests to the first water electrolysis plateau followed by a second plateau due to carbon corrosion at the anode [73, 5, 14, 26, 74, 75, 67, 68]. No carbon corrosion plateau was evident in these subfreezing temperature tests. Instead, following the water electrolysis plateau, we generally saw significant decreases in cell voltage due to capacitive charging of the anode rather than Faradaic reactions. In cases where we allowed sustained current density at these large voltages (negative cell, positive anode voltage), we would see a voltage plateau that we have attributed that to self-heating of the cell and likely the melting of ice and thermal activation of carbon corrosion.

5.3.2 Hydrogen-pumping cell reversal experiments

To eliminate the ice formation effects due to the ORR at the cathode in well-controlled experiments, we performed the hydrogen-pumping cell reversal experiments using 0 wt% and 5 wt% RTA MEAs. When the current was applied to the hydrogen-pumping cell, there was only HER at the cathode instead of ORR. In this case, the cathode had a negligible overpotential due to the fast HER kinetics and no problematic water generation in the absence of oxygen. Thus, the anode is the primary source of any changes of cell voltage.

Repeated hydrogen-pumping cell reversal tests of 0 wt% RTA MEA at -5°C

Figure 5.2 shows the repeated hydrogen-pumping cell reversal test results of 0 wt% RTA MEA at -5°C. We repeated reversal tests on the same MEA at two different anode gas flow rates: 134 and 1000 ml/min. We studied the humidified gas flow rate since it changes the amount of water delivered to support OER and also shows whether freezing of the water in the supply gases affects the results.

Figure 5.2a shows the cell voltage changes during the 0.2 A/cm² hydrogen-pumping cell reversal tests as a function of time. At the beginning of the hydrogen-pumping cell tests, as mentioned before in the Experimental section, the anode and cathode were firstly supplied with hydrogen and nitrogen, respectively. In this case, the half-cell reactions are the hydrogen oxidation reaction (HOR) at the anode, and the HER at the cathode due to the absence of oxygen, and the overall cell voltage was around 0 V. The anode gas feed was then switched to nitrogen, which caused a sudden drop of the cell voltage to around -2 V. We attribute the voltage plateaued at -2 V to OER dominated reactions at the anode. The plateau lasted for roughly 50 s followed by a voltage drop down to -4.5 V when the reversal experiment terminated. It is noteworthy that no plateau representing the carbon corrosion reaction (COR) dominated region was observed during hydrogen-pumping cell reversal tests at -5°C, similar to the hydrogen-air cell experiments. Again, this is in contrast to COR dominated plateaus that usually observed during reversal tests at higher temperatures (e.g., 65°C and 90°C) in a cell voltage range of approximately -1.5 to -2.0 V [5, 14]. Although there was approximately a seven-fold difference of the anode gas flow rates between 134 and 1000 ml/min, no significant change in the voltage reversal time duration was observed. Thus, we are confident that the loss of OER current after 50 s and the lack of a COR voltage plateau is not due to water starvation from under-delivery of water vapor in the nitrogen. Also, though two different gas flow rates were used, there

is no significant difference in the timing of the cell voltage's sudden drop, indicating that the cell voltage change is not likely to be caused by icing of water vapor from inlet gases.

The polarization curves were obtained at beginning of life (BOL) and after each hydrogen-pumping cell reversal test as shown in Figure 5.2b. Though the cell experienced repeated reversal tests, the polarization curves after each reversal almost overlap each other. Only a slight decrease of cell voltage in the mass transport loss region at high current densities, i.e., from 1.2 to 1.6 A/cm², was observed. Prior work by Mandal *et al.* [5] with the same type of MEA and cell reversal testing protocols at a high temperature, 65°C, showed that the cell voltage at 1.2 A/cm² decreased by 70% within 2.2 min of accumulated cell voltage reversal time. In contrast, for the repeated cell reversal tests at -5°C, from the polarization curves, the cell voltage decreased by less than 5 % after 5 min of cell voltage reversal time.

Figure 5.2c shows the anode CV curves. As the hydrogen-pumping cell reversal tests proceeded, there was a continuous decrease of hydrogen desorption (anodic) and adsorption (cathodic) peaks at around 0.1 - 0.3 V as well as the Pt oxide formation (anodic) and oxide reduction (cathodic) peaks in the range of 0.7 - 0.9 V [76], indicating a minor loss of electrochemical active surface area (ECSA). However, this loss of ECSA with subfreezing temperature reversals is more likely to be caused by Pt catalyst degradation or freeze-thaw damage rather than massive carbon corrosion damage at high anode overpotentials, since the CV peak frequently observed at around 0.5 - 0.7 V due to the hydroquinone-quinone (HQ-Q) redox reaction [5, 14, 60, 77], which is commonly used as an indicator for drastic COR at high anode potentials, is hardly seen in these CV results. Figure 3d shows the corresponding EIS Nyquist plots recorded at current densities of 0.1 and 0.4 A/cm². The Nyquist plots are almost all identical for each current density after successive reversals, showing a negligible increase in the charge transfer resistance (i.e., semi-circles' apparent radius) and high frequency resistance (HFR) (i.e., first real-axis intercept). In our previous study of cell reversal at higher temperature of 65°C, the cell HFR increased from

0.07 ohm.cm² to 0.39 ohm.cm² within 2.2 min of accumulated voltage reversal time, and significant change in the anode charge transfer resistance ($R_{ct,an}$) can be observed. In contrast, there is negligible change in HFR and $R_{ct,an}$ for cell voltage reversals at -5°C. Admittedly, there might be coexistence of COR and OER at the voltage potential plateau of -2 V during reversal tests at -5°C. However, the minimal cell voltage decrease, HFR and $R_{ct,an}$ increases compared with high temperature reversals in our prior work [5], indicate a heavily suppressed COR at subfreezing temperatures.

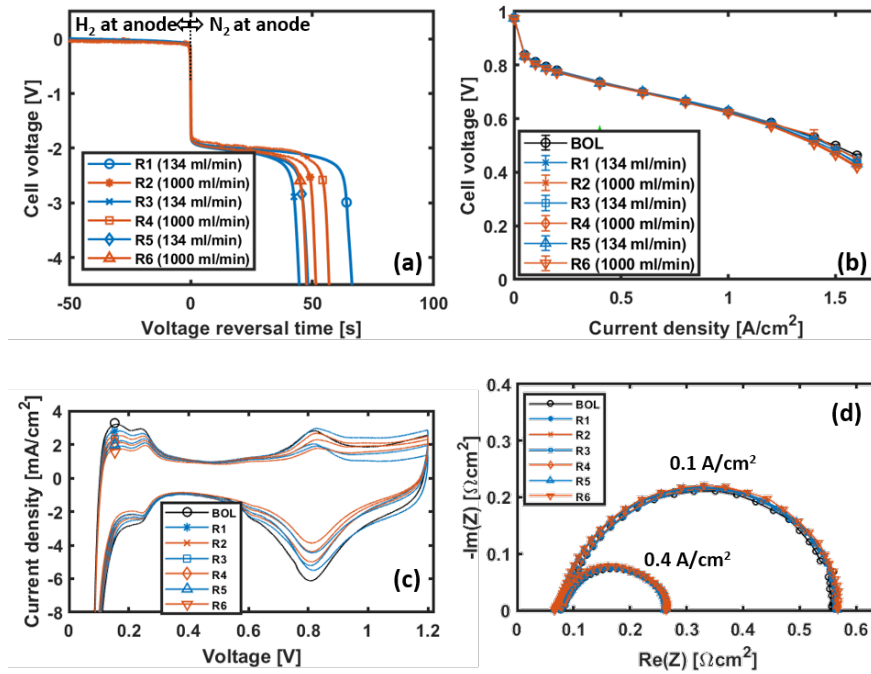


Figure 5.2: Repeated hydrogen-pumping cell reversal test results at -5°C using 0 wt% RTA MEA with an alternating gas flow rate between 134 ml/min (R1, R3 and R5) and 1000 ml/min (R2, R4 and R6) and characterization at BOL and after each reversal. (a) The cell voltage changes during hydrogen-pumping cell tests. (b) Polarization curves. (c) Anode CV. (d) EIS Nyquist plots for current densities of 0.1 and 0.4 A/cm². Reprinted with permission from [3], Copyright(2020), American Chemical Society.

Temperature-dependent hydrogen-pumping cell reversal study

To better examine the effect of temperature on suppressing cell reversal degradation, we performed hydrogen-pumping cell reversal measurements with consecutively increasing temperature during each. Furthermore, to elucidate the efficiency of RTAs as a function of temperature, we carried out these experiments on both 0 wt% and 5 wt% RTA MEAs. Figure 5.3a shows the temperature-dependent hydrogen-pumping cell reversal test results of the 0 wt% RTA MEA. The reversal tests were conducted for cell temperatures ranging from -15 up to 20°C. For the test at -15°C, after the cell voltage reverses (i.e., $E_{\text{cell}} \downarrow 0$ V), the cell voltage plateaus at around -2 V, according to the water electrolysis reaction. As we increased the temperature in subsequent reversals, the voltage reversal time duration at the first plateau accordingly increases, from 18 s at -15°C to 63 s at 5°C. In this temperature range, we did not observe a secondary plateau due to carbon corrosion, and the anode voltage became very large following the electrolysis plateau. As the temperature further increases from 10 up to 20°C, however, the reversal time decreases with the advent of a second plateau in the range of -2.5 to -3.5 V, which we believe is due to the emergence of COR sustaining the applied current density. Post-reversal electrochemical characterizations are supporting this observation and will be discussed later.

To examine the effectiveness of the IrO₂ RTA in postponing the carbon corrosion reaction at low temperatures, we conducted the same study with a 5 wt% RTA MEA. Figure 5.3b shows the voltage time series for reversal tests that were conducted for temperatures ranging from -15 to 45°C. The cell voltage during reversal at -15°C shows the first plateau at around -2 V for 20 s. In the case of 5 wt% RTA MEA, the voltage reversal duration time at the first plateau representing the water electrolysis reaction generally increases with increasing the reversal temperature from -15 to 20°C, with the longest water electrolysis time of 140 s observed at 20°C. This behavior is quite distinct from cell reversals with

the 0 wt% RTA MEA, which exhibited the second plateau of carbon corrosion from 10 to 20°C and maximum first plateau reversal times of 63 s. As the reversal temperature keeps increasing from 25 to 45°C, the water electrolysis time of the 5 wt% RTA MEA decreases from 100 s at 25°C to around 30 s at 45°C. Figure 5.3c shows the comparison of the voltage reversal times of 0 wt% and 5 wt% RTA MEAs as a function of the reversal test temperature. By adding IrO₂ RTA, a longer water electrolysis time was achieved at low temperatures above freezing (i.e., 10 - 45°C) and the second plateau for the COR was not observed until reaching a temperature of 45°C after several consecutive reversals. It's noteworthy that although a second plateau due to carbon corrosion of the 5 wt% RTA MEA was not observed for temperatures from 25 to 45°C, we cannot fully exclude the possibility of the minor contribution of carbon corrosion to the overall reversal degradation and reduced duration of the water electrolysis plateau in this temperature range. The prolonged water electrolysis time of the 5 wt% RTA MEA suggests that the IrO₂ in the RTA enhanced the water electrolysis reaction, suppressing the onset of carbon corrosion reaction.

The increasing voltage reversal time as the temperature is increased from -15 to 0°C (see Figure 5.3c) is an intriguing finding. Our present understanding from these results is that the end of the water electrolysis plateau is due to local water starvation in the freezing condition. As the temperature increases, there is a greater fraction of unfrozen water in the polymer electrolyte and greater water mobility in the anode that extends the period before the OER is water starved. The subsequent decrease in water electrolysis reversal time at higher temperatures is likely due to initially minor poisoning of the Pt (i.e., 0 wt% RTA MEA) or Pt and IrO₂ (i.e., 5 wt% RTA MEA) catalysts by small amounts of carbon corrosion products as we have postulated in our prior work [5, 14].

Figure 5.4a (1-3) present detailed electrochemical analyses that were carried to investigate the cell degradation mechanisms due to the carbon corrosion during hydrogen-

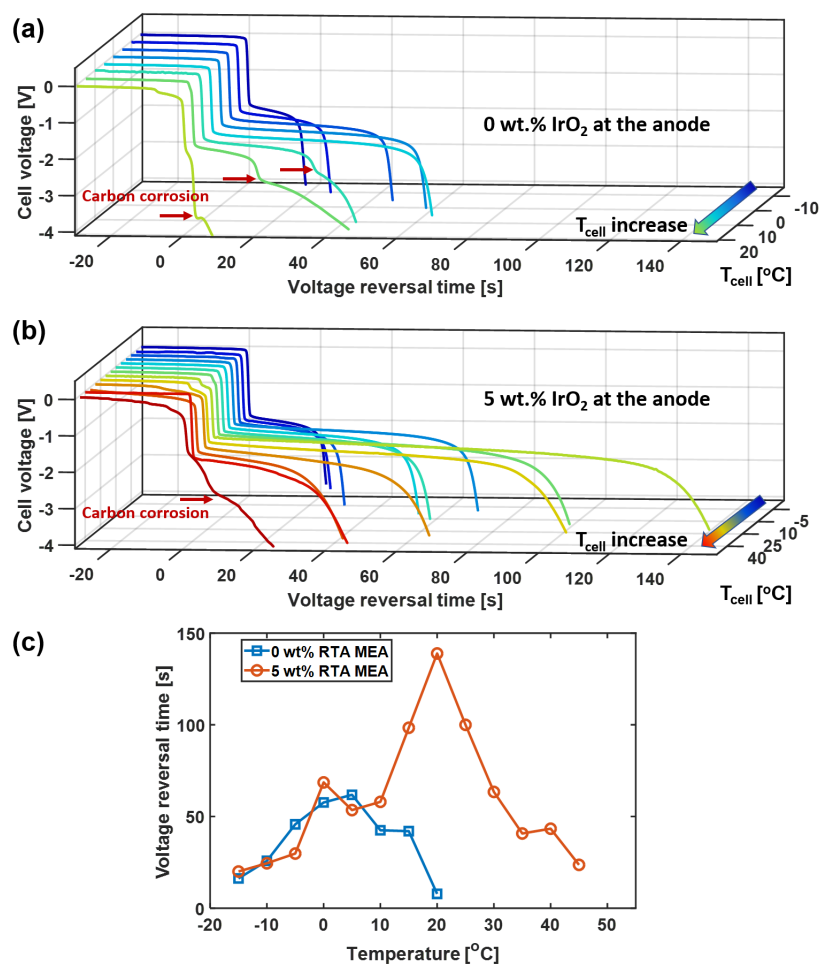


Figure 5.3: Temperature-dependent cell voltage change during hydrogen-pumping cell reversal tests. (a) Cell reversal test results of 0 wt% RTA MEA from -15 to 20°C. (b) Cell reversal test results of 5 wt% RTA MEA from -15 to 45°C. (c) Comparison of the voltage reversal time between 0 wt% and 5 wt% RTA MEAs as a function of the reversal test temperature. Reprinted with permission from [3], Copyright(2020), American Chemical Society.

pumping cell reversals at varying temperatures with and without IrO₂ in the anode. Figure 5.4a-1 shows the CV curves of the 0 wt% RTA MEA at BOL and after each hydrogen-pumping cell reversal test. The CV curve in black represents the BOL state. From -15 to 5°C, both the hydrogen desorption peaks at around 0.1 - 0.3 V and Pt oxide formation peaks at around 0.7 - 0.9 V decreased. The decrease of these characteristic peaks shows a similar trend to the CV results of repeated hydrogen-pumping cell reversals at -5°C in Figure 5.2c, which could be attributed to freeze-thaw damage. In the case of the hydrogen-pumping cell reversal test at 10°C, another characteristic peak began to evolve in the range of 0.5 - 0.7 V, which corresponds to HQ-Q redox peak [5, 14, 60, 76, 77] and indicating drastic carbon corrosion reaction. This carbon corrosion peak became larger after the reversal tests at 15 and 20°C, suggesting an increased extent of carbon surface oxidation. Figure 5.4a-2 presents the polarization curves of the 0 wt% RTA MEA at BOL and after each hydrogen-pumping cell reversal test. After the hydrogen-pumping cell reversal tests in the temperature range of -15 to 5°C, we only observed slight voltage decreases at current densities higher than about 1.2 A/cm² (mass transport loss region). At higher reversal temperatures of 10 - 20°C, however, more pronounced voltage decreases were observed over the entire polarization curve, including at lower (i.e., activation loss region) and medium (i.e., ohmic loss region) current densities. As shown in Figure 5.4a-3, the increase in ohmic resistances after the hydrogen-pumping cell reversal tests at 10 - 20°C was clearly observed in the EIS Nyquist plots, indicating an increased contact resistance in the MEA. Our prior work has shown that this is due to a depletion of carbon at the anode's interface with the membrane [5, 14].

Figure 5.4b-1 shows the CV curves of the 5 wt% RTA MEA at BOL and after each hydrogen-pumping cell reversal test. Similar to the characterization results of 0 wt% RTA MEA in Figure 5.4a-1, both the hydrogen desorption and Pt oxide formation peaks decreased. However, the carbon corrosion peaks at around 0.5 - 0.7 V due to the HQ-Q

redox reaction did not substantially appear until the highest temperature of 45°C, implying that the IrO₂ catalyst in the anode suppressed the COR up to this temperature. Figure 5.4b-2 shows the polarization curves of the 5 wt% RTA MEA at BOL and after each hydrogen-pumping cell reversal test. After the hydrogen-pumping cell reversal tests in the temperature range of -15 to 20°C, we only observed voltage decreases in the mass transport loss region. At higher reversal temperatures of 25 - 45°C, severe voltage losses were observed in both the activation and ohmic loss regions. As Figure 5.4b-3 shows, the ohmic resistance increased significantly at the highest test temperature of 45°C, indicating a significant loss of carbon at the anode's membrane interface.

As the electrochemical diagnostics in Figure 5.4 show, the use of an RTA with an OER catalyst significantly reduces the rate of degradation, particularly at temperatures above freezing. Figure 5.5a-b summarize the changes of the cell voltage after each reversal for the 0 wt% and 5 wt% RTA MEAs. The cell voltage values were taken at a current density of 0.4 A/cm² and were normalized based on the BOL cell voltage at the same current density. Figure 5.5a is the normalized cell voltage vs. cell reversal temperature. We can see that for both 0 wt% RTA MEAs, the normalized cell voltages after reversal tests in freezing conditions show no significant change. However, the cell voltage decay becomes evident when the cell reversal temperature is above 5°C for 0 wt% RTA MEA and above 20°C for 5 wt% RTA MEA. Figure 5.5b shows the normalized cell voltage vs. accumulated cell voltage reversal time. For the 0 wt% RTA MEA, the cell voltage starts to distinctly decrease at around 250 s of accumulated cell voltage reversal time. In contrast, the cell voltage of 5 wt% RTA MEA decreases significantly at about 590 s of accumulated voltage reversal time. Both Figure 5.5a and b indicate that there was negligible COR damage to anodes when the fuel cell's voltage was reversed in freezing conditions for both 0 wt% and 5 wt% RTA MEAs. When exposed to temperatures sufficiently higher than 0°C, however, the fuel cell with the 5 wt% RTA MEA degraded significantly less than 0

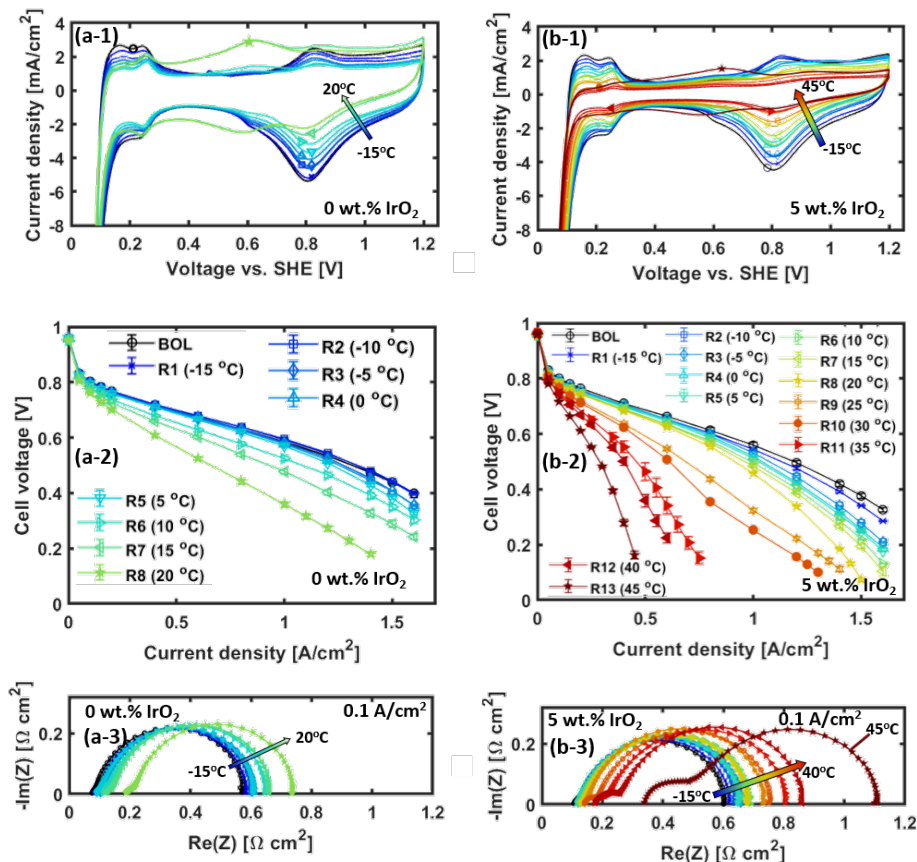


Figure 5.4: Post-characterization results after the temperature-dependent hydrogen-pumping cell reversal. Anode CV curves for (a-1) 0 wt% and (b-1) 5 wt% RTA MEAs. Polarization curves for (a-2) 0 wt% and (b-2) 5 wt% RTA MEAs. EIS Nyquist plots at 0.1 A/cm² for (a-3) 0 wt% and (b-3) 5 wt% RTA MEAs. Reprinted with permission from [3], Copyright(2020), American Chemical Society.

wt% RTA MEA, implying the effectiveness of the IrO₂ RTA catalyst for suppressing the COR at anodes.

To examine the voltage reversal damage to the morphology of anode catalyst layers, SEM images and EDS spectra were taken from the cross sections of the pristine and reversal-tested MEAs, and are shown in Figure 5.4c-d. The average anode thickness of the BOL 0 wt% RTA MEA was 3.0 μm based on SEM images in Figure 5.4c. The 0 wt% RTA MEA after repeated reversal tests at -5°C showed a negligible anode thickness change. However, the anode thickness of 0 wt% RTA MEA after repeated reversal tests with increasing cell temperature decreased to 2.5 μm , i.e., approximately 17% of reduction. The change in anode thicknesses is due to the carbon corrosion and partial collapse of the anode when the cell was reversed at temperatures above freezing. This observation is supported by EDS spectra and the change in the element weight percentage. As Figure 5.4c shows, there is no significant element weight percentage change for the 0 wt% RTA sample after repeated tests at -5°C. In contrast, there is a notable increase in the relative weight of Pt vs. carbon when the reversal temperature was increasing due to the loss of carbon. This trend is much clearer in Figure 5.4d that shows the results for the 5 wt% RTA MEA sample after repeated reversal tests with increasing cell temperature, where the ratio of Pt to carbon is dramatically increased due to the anode being exposed to more facile carbon corrosion conditions for a more extended period.

5.4 Conclusions

In this study, we have investigated cell reversal degradation from -15 to 45°C through electrochemical diagnostics, including the use of an integrated reference electrode. We examined both conventional anodes and RTAs with OER catalyst added. From the hydrogen-air cell freezing reversal tests at -15°C, we observed substantially a different cell voltage time

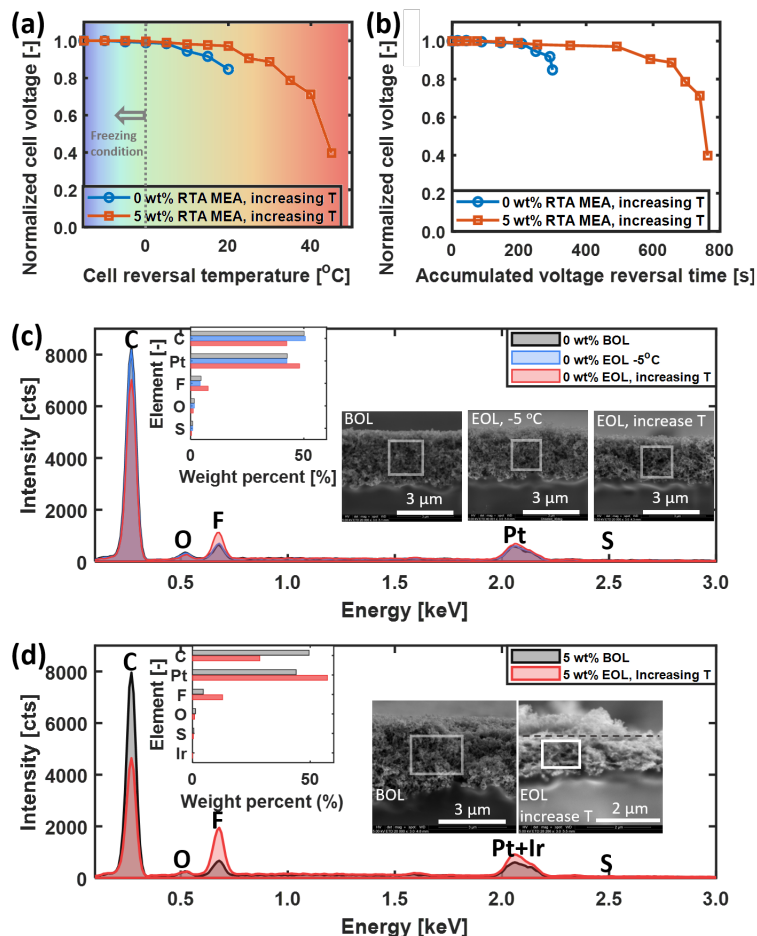


Figure 5.5: The change of normalized cell voltage at 0.4 A/cm^2 vs. cell reversal temperature (a) and accumulated voltage reversal time (b). (c) Cross-sectional SEM images and EDS spectra of anodes of the 0 wt% RTA MEAs without any reversal test (0 wt% BOL), after repeated reversal tests at -5°C (0 wt% EOL -5°C) and after repeated reversal tests with increasing cell temperature (0 wt% EOL increasing T). (d) Cross-sectional SEM images and EDS spectra of anodes of the 5 wt% RTA MEAs without any reversal test (5 wt% BOL) and after repeated reversal tests with increasing cell temperature (5 wt% EOL increasing T). Reprinted with permission from [3], Copyright(2020), American Chemical Society.

series from previously reported high-temperature reversal tests. Using the reference electrode, we observed that the anode potential exhibited an increase to a single voltage plateau consistent with water electrolysis reaction. The single voltage plateau is followed by a significant voltage increase to ~ 2 V due to capacitive charging, without any indication of the carbon corrosion voltage plateau observed at normal operating temperatures. Repetitive hydrogen-pumping cell reversal tests of the MEA at a constant subfreezing temperature of -5°C revealed no significant changes in terms of fuel cell polarization curve and EIS spectra. In contrast, repeated hydrogen-pumping cell reversal tests with consecutive temperature increases from -15 to 20°C (conventional anode MEA) or 45°C (for 5 wt% RTA MEA), we found the carbon corrosion was highly suppressed at temperatures of 0°C and lower for both MEAs. At 10°C and above, the carbon corrosion became apparent with the conventional anode. With the addition of IrO_2 OER catalyst (5 wt% RTA MEA), we found significantly increased reversal times and suppression of carbon corrosion at higher temperatures ($\sim 40^{\circ}\text{C}$). We also observed that the duration of the water electrolysis plateau decreased at the lower temperatures below freezing. This is likely due to the limited availability of water that is governed by the unfrozen fraction of the water and its mobility. These findings are encouraging for the development of polymer electrolyte membrane fuel cell (PEMFC)s that can be robustly operated in subfreezing conditions. Despite the negligible carbon corrosion at subfreezing condition, the temperature dependence of that carbon corrosion indicates the need for an RTA to prevent carbon corrosion as the cells warm up during initial operation.

Chapter 6

Understanding Cell Reversal Damage: Towards Reversal Tolerant Anode

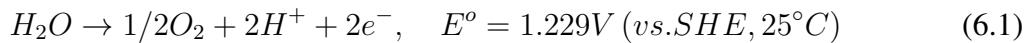
6.1 Introduction

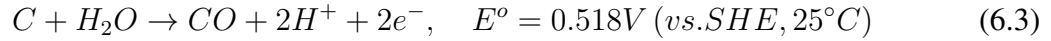
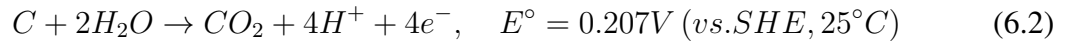
This chapter will present the works on the development of the reversal invincible anode (RIA). fuel cell electric vehicle (FCEV)s powered by polymer electrolyte membrane fuel cell (PEMFC)s need an improvement in their durability and robustness to achieve broader commercialization. The cell reversal induced by hydrogen starvation could significantly reduce the performance and durability of the PEMFC system in a short time. Here we present the cell performance degradation and cell failure mechanisms during hydrogen starvation through examining membrane electrode assembly (MEA) with several different anode structures. For an MEA with conventional anode composed of carbon supported Pt catalyst (Pt/C), the degradation caused by cell reversal primarily comes from the carbon support corrosion. It is noteworthy that an MEA with Pt black-only anode without any carbons also fails during hydrogen starvation. It is postulated that cell failure and performance degradation of the MEA with Pt black-only anode are caused by the corrosion of carbon materials present at the anode microporous layer (MPL) in gas diffusion layers.

Based on these findings, we propose RIAs composed of both Pt black as a catalyst layer and thin titanium (Ti) as a protective layer. The conventional MEA with platinum (Pt) anode exhibits the highest cell voltage degradation rate of 15.2% loss/min and the lowest reversal tolerance, whereas the RIA MEA with Pt black and 13.0 μm -thick Ti layer anode performs the lowest cell voltage degradation rate of 0.045% loss/min and the highest reversal tolerance which is approximately 340-fold increase compared with the conventional MEA with Pt/C anode. These findings will greatly contribute to designing a new concept of RIAs and enhancing the cell voltage reversal tolerance of PEMFCs dramatically under severe operating conditions of hydrogen starvation and thus perfecting the competitiveness of FCEVs.

6.1.1 Hydrogen starvation and carbon corrosion at high operating temperatures

For a normally operating fuel cell, hydrogen is sufficiently supplied to the anode. Because of the fast kinetics of the hydrogen oxidation reaction (HOR), the anode potential is low. Hydrogen starvation could happen when there is a sudden increase in the power demand, anode flooding, or when there is nitrogen accumulation at the anode [5]. During hydrogen starvation, the anode potential (E_{an}) increases higher than the cathode potential (E_{ca}), and thus the cell voltage (E_{cell}) eventually reverses, i.e., $E_{\text{cell}} = E_{\text{ca}} - E_{\text{an}} < 0\text{V}$, as illustrated in the stage 1 of Figure 6.1. As the potential of anode increases significantly, i.e., $> 1.229\text{ V}$, the anode is subject to perform an oxygen evolution reaction (OER) as shown in equation 1 and carbon corrosion (or oxidation) reaction (CCR) as shown in Equations 6.2 and 6.3.





where E_0 is the standard reversible potential versus the standard hydrogen electrode (SHE).

Though CCR is thermodynamically favorable with lower reversible potentials, it has sluggish kinetics [78]. As illustrated in the stage 2 of Figure 6.1, at the start of the hydrogen starvation and cell voltage reversal, the anode will temporarily remain at the OER dominated region. However, at high anode potentials, there is still a trace amount of carbon corrosion, which leads to the temporary deactivation of the anode catalyst that sustains the OER [79]. As the anode catalyst is temporarily deactivated, the cell voltage will further decrease, as shown in the stage 3 of Figure 6.1, and the anode will be in CCR dominated region (stage 4 of Figure 6.1), and the cell will eventually fail (stage 5 of Figure 6.1). This transient cell reversal behavior has been reported and studied by a lot of researchers [3, 14, 5, 80, 73, 27, 81].

Though adding OER catalyst or using more corrosion-resistant catalyst support has been proven to be effective to increase the anode durability, these conventional approaches usually suffer from a limited lifetime under hydrogen starvation conditions [14, 5, 27]. As the cell voltage reversal tolerance under hydrogen starvation conditions is essential to the broad commercialization of FCEVs, it will be beneficial to have a highly robust anode that can maintain a stable OER reaction and is less vulnerable to electrode damage during hydrogen starvation, that is, a RIA. In this study, we have examined the reversal

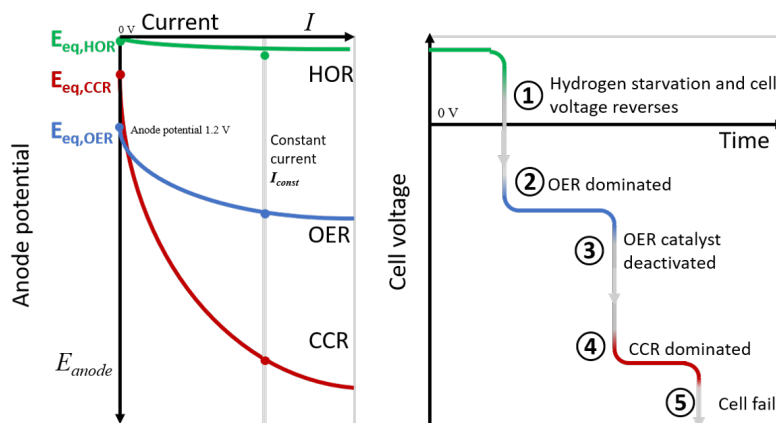


Figure 6.1: Schematic of different anode reactions and the corresponding transient cell voltage behavior during hydrogen starvation.

tolerance of membrane electrode assemblies (MEAs) with three different anode structures to understand the cell reversal damage to the anode, the cell failure mechanism, and thus propose a new design concept of RIAs.

6.2 Experimental

6.2.1 MEA preapration

The MEAs were fabricated using a perfluorosulfonic acid (PFSA) ionomer membrane (Nafion[®] NRE115 (H⁺) form, DuPont, USA). The cathodes of all three types of MEA samples and the anode of the benchmark MEA sample were made of gas diffusion electrode (GDE)s (0.3 mg_{Pt}/cm² of 40 wt% Pt/C (Vulcan) on carbon paper from Fuel Cells Etc. company, College Station, USA). The gas diffusion layer (GDL) used for GDE was composed of both macro-porous substrate (MPS) and MPL. The benchmark MEA sample using the anode made of GDE (as shown in Figure 6.2a) is referred to as ‘MEA with Pt/C anode’ throughout this study. For the other two MEA samples, the anode Pt black catalyst

inks were prepared by dispersing Pt black (95+ wt%, HiSPEC 1000, Johnson Matthey Fuel Cells, Swindon, UK) and PFSA ionomer binder (Alcohol-based 5 wt% Nafion[®] D521 Dispersion, Equivalent Weight = 1100 g/eq., Fuel Cell Store, College Station, Texas, USA) into isopropanol (IPA). The Pt black to dried Nafion[®] ionomer binder weight ratio was 20:1. The catalyst ink was ultrasonicated for 1 hr before directly coated on the anode side of the PFSA membrane. The loading of the Pt black at anode was also 0.3 mg_{Pt}/cm², the same as that of the commercial GDE used for the benchmark anode. For the MEA using an anode with Pt black only as the catalyst layer (referred to as ‘MEA with Pt black-only anode’ sample, as shown in Figure 6.2b), a commercial GDL consisting of both MPS and MPL (25 BC, 5 wt% polytetrafluoroethylene (PTFE) in MPS, Sigracet of SGL GmBH, Fuel Cells Etc., College Station, USA) was put on top of the anode. For the MEA using an anode consisting of both Pt black and a thin Ti layer (referred to as ‘MEA with Pt black + Ti layer anode’ sample, as shown in Figure 6.2c), the same type of anode GDL of 25BC was also used. On top of the anode MPL, a thin Ti layer was generated through a sputtering method. In this study, two Ti layers with different thicknesses of 4.8 μm and 13.0 μm were examined. For all the three MEA samples with different anode structures, the active areas of both cathodes and anodes were fixed to be 1 cm².

6.2.2 Preconditioning

Before testing each MEA under hydrogen starvation conditions, the MEA was preconditioned to achieve a stabilized cell performance. The preconditioning was conducted at 65% and 100% relative humidity (RH). Hydrogen to the anode and air to the cathode were both supplied at a flow rate of 200 ml/min. During the preconditioning, the cell was cycled at 0.8 V, 0.5 V, and 0.3 V repeatedly for 5 min hold at each voltage until the cell current was stable. The temperature and gas flow rates were controlled by a commercial fuel cell test station (850 Test stand, Scribner Associates Inc., North Carolina, USA).

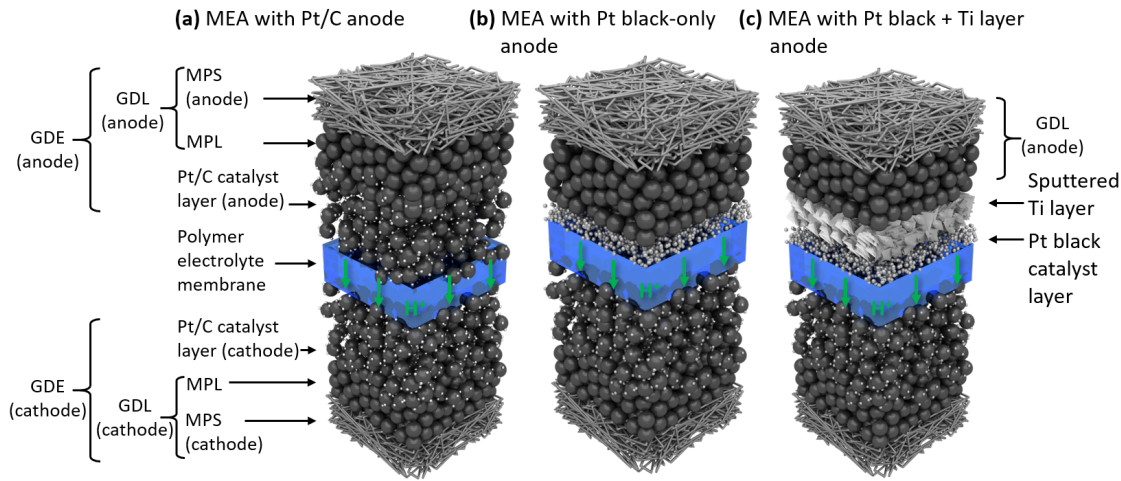


Figure 6.2: Schematic of three MEAs with different anode structures: (a) MEA with Pt/C anode; (b) MEA with Pt black-only anode; (c) MEA with Pt black + Ti layer anode. The cathode sides of all the three MEAs adopted the same GDEs.

The electrochemical measurements were conducted using a potentiostat (VSP, Bio-Logic, Claix, France).

6.2.3 Hydrogen starvation test

During the hydrogen starvation test, the cell temperature and RH were 65 °C and 100%, respectively. At the beginning of the hydrogen starvation test, fully humidified hydrogen at a flow rate of 200 ml/min was separately supplied to both the anode and the cathode. In previous hydrogen starvation studies, the cathode was usually supplied with air [14, 5]. Supplying hydrogen to the cathode turns the cathode into a stable reference point and makes it easier to monitor the anode potential change during cell reversal tests. Then the cell was operated at a constant current density of 0.2 A/cm². The anode was in the hydrogen environment for 2 min before switching the anode gas supply from hydrogen to nitrogen at the same gas flow rate to simulate the hydrogen starvation. It took about 3

min until the hydrogen starvation affected the cell voltage since the hydrogen/nitrogen gas boundary had to go through the internal gas lines inside the fuel cell test stand. The cell voltage was monitored throughout the tests and a cutoff voltage of -2.5 V was employed for cell reversal tests.

6.2.4 Electrochemical characterization

After the preconditioning followed by each hydrogen starvation test, we characterized different cells at 65°C and 100°C RH. cyclic voltammetry (CV) measurements were conducted at the anode, with the anode being supplied with nitrogen at 200 ml/min and the cathode being provided with hydrogen at 200 ml/min. The voltage range for the CV scans was from 0.04 to 1.2 V at a scan rate of 50 mV/s. For electrochemical impedance spectroscopy (EIS) and polarization curve measurements, the anode was supplied with hydrogen at 200 ml/min, and the cathode was supplied with air at 200 ml/min. EIS measurements were performed with the potentiostatic mode at a cell voltage of 0.5 V.

6.2.5 Scanning electron microscope (SEM) characterization

The MPL and Ti protection layer were imaged using an scanning electron microscope (SEM) instrument (Quanta 600 FEG, FEI Company, OR, USA) with the secondary electron detector. The working distance is 8.6 mm at an accelerating voltage of 10 kV and a spot size of 3.

6.3 Results and discussion

6.3.1 Hydrogen starvation tests of the MEA with Pt/C anode

Figure 6.3 presents the hydrogen starvation test results for the MEA with Pt/C anode. Figure 6.3a shows the change of cell voltage during the hydrogen starvation test. As we can see, when the anode gas was switched from hydrogen to nitrogen, it took about 3 min until a sudden drop of the cell voltage occurred, which corresponds to the cell voltage reversal process. After the sudden drop, the cell voltage leveled off at potentials in the range of -1.8 V to -2.0 V for a short period of time, and then it further dropped to the cutoff voltage limit of -2.5 V. For the 1st reversal test, the voltage reversal time is around 2.5 min. The voltage reversal time becomes shorter as the repeated reversal tests continue. Figure 6.3b shows the anode CV curves. Compared with the initial beginning of life (BOL) CV curve, one distinct change in the CV curves after each reversal test is that new peaks appear in the range of 0.5 V to 0.7 V. These unique peaks are caused by the hydroquinone-quinone (HQ-Q) redox reaction and are generated by carbon corrosion at high potentials [14, 5, 3, 60, 77]. It should be noted that slow carbon corrosion reaction at low anode potentials would not cause HQ-Q peaks in CV curves, such as in open circuit voltage (OCV) conditions. In the present study, we used the evolution of HQ-Q peaks as an indicator of extensive carbon corrosion at high anode potentials.

Figure 6.3c presents the Nyquist plots of the electrochemical impedance spectroscopy (EIS) results. It reveals that the ohmic or high frequency resistance (HFR), which is the intercept of the left side of each curve with the real axis (Re_Z), increases with the consecutive reversal tests. The overall charge transfer resistance which consists of both anode's charge transfer resistance (i.e., the higher frequency semicircle on the left side) and cathode's charge transfer resistance (i.e., the lower frequency semicircle on the right side) also

increases significantly after repeated reversal tests. Figure 6.3d shows the polarization curves. At 0.4 A/cm^2 , it is found that the cell voltage of the conventional MEA with Pt/C anode drops from 0.48 V at BOL to 0.08 V after an accumulated voltage reversal time of 5.5 min, corresponding to a degradation rate of $15.2\%/min$. The increase of HQ-Q redox peaks from CV results suggests a significant amount of carbon corrosion at the anode. The observed increase in both HFR and charge transfer resistance indicates severe damage to the electrodes caused by cell reversals. The increased activation loss from the polarization curve also suggests significant electrode damage.

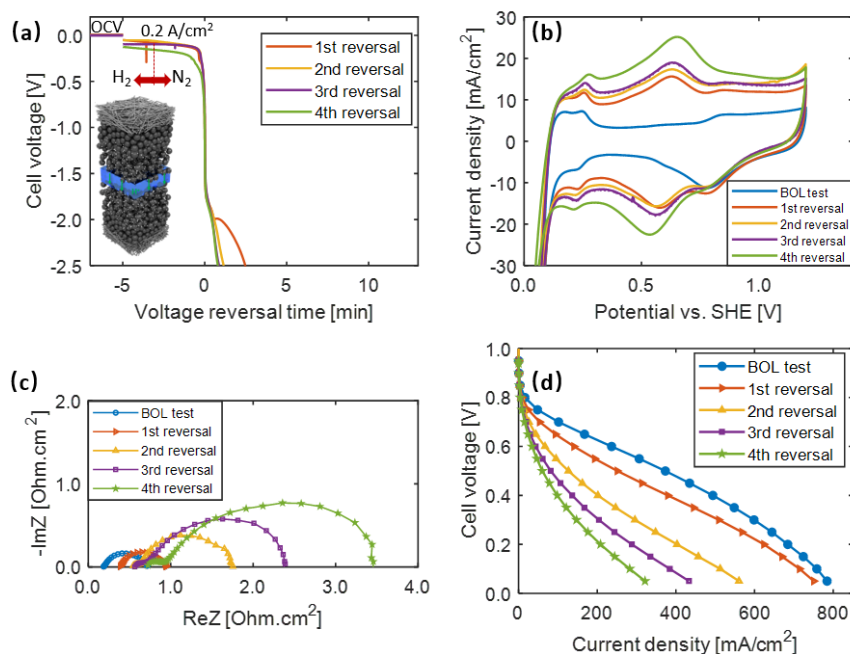


Figure 6.3: Repeated hydrogen starvation test results of the MEA with Pt/C anode. (a) The change of cell voltage during hydrogen starvation. (b) Anode CV curves after pre-conditioning and each reversal test. (c) EIS Nyquist plots at a cell voltage of 0.5 V. (d) Polarization curves.

6.3.2 Hydrogen starvation tests of the MEA with Pt black-only anode

In comparison, Figure 6.4 shows the hydrogen starvation results for the MEA with Pt black-only anode. Figure 6.4a shows the cell voltage change during each hydrogen starvation test. Though only Pt black without any carbon supports is used as the anode catalyst, it is still observed that the cell voltage reached the cutoff voltage limit of -2.5 V in a short time. For the first hydrogen starvation test, the cell lasted about 3.8 min in cell reversal state, slightly longer than the MEA with Pt/C anode. Similar to that of the MEA with Pt/C anode, the cell voltage of the MEA with Pt black-only anode dropped quickly as the hydrogen starvation test continued. Interestingly, in the anode CV results shown in Figure 6.4b, HQ-Q peaks at around 0.6 V are still pronounced after repeated hydrogen starvation tests, which suggest the carbon corrosion reaction at high anode potentials. In the EIS results shown in Figure 6.4c, it is observed that the increases in both charge transfer resistance and ohmic resistance of the MEA with Pt black-only anode are much smaller than those of the MEA with Pt/C anode. In the polarization curves shown in Figure 6.4d, it is found that the cell performance degradation pattern with continuing the reversal tests of the MEA with Pt black-only anode is different from that of the MEA with Pt/C anode. The cell performance loss mainly comes from the ohmic and the mass transfer loss regions. Based on these electrochemical characterizations, it is likely that the carbon at the anode MPL became corroded during hydrogen starvation, which caused the HQ-Q peaks in the CV curves. The corrosion of MPL that is in contact with the catalytic Pt-black layer can increase the HFR, since the loss of carbon in MPL increases the electrical contact resistance between the MPL and the catalytic Pt-black layer. It has been reported that a trace amount of carbon corrosion could lead to the temporary deactivation of anode catalyst layer that sustains the OER reaction [79]. The corrosion of the MPL can also explain the unstable OER and quick cell failure under hydrogen starvation conditions.

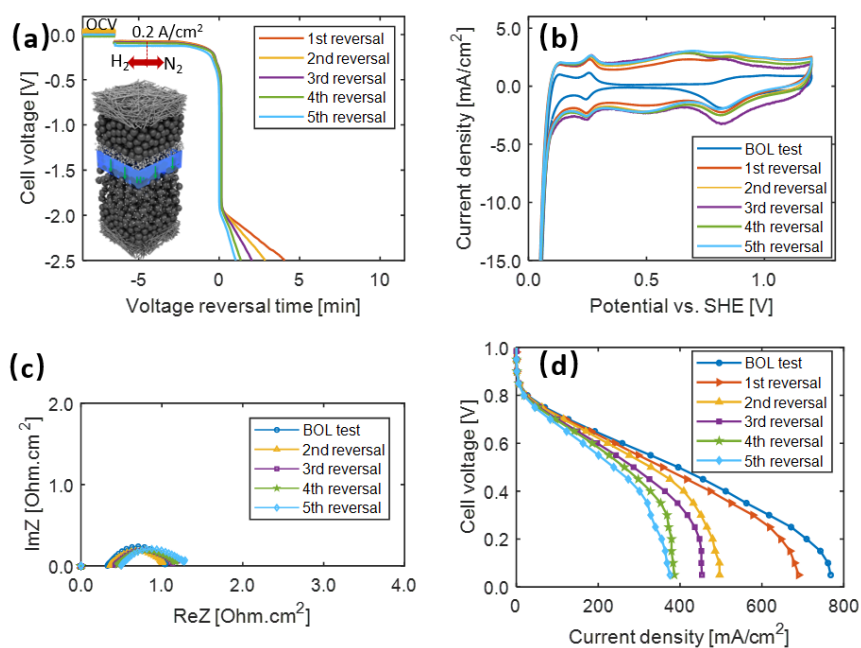


Figure 6.4: Repeated hydrogen starvation tests of the MEA with Pt black-only anode. (a) The change of cell voltage during hydrogen starvation. (b) Anode CV curves after preconditioning and each reversal test. (c) EIS Nyquist plots at a cell voltage of 0.5 V. (d) Polarization curves.

6.3.3 Hydrogen starvation tests of the MEA with Pt black + Ti layer anode

The motivation of using Ti layer is to protect the MPL from corrosion during hydrogen starvation. Two different Ti layer thicknesses were tested and examined, i.e., 4.8 μm and 13.0 μm . Figure 6.5 shows the side and top views of the sputtered 13.0 μm Ti protection layer on the MPL. From the SEM images, the generated Ti layer appears very uniform in thickness. From the zoomed-in side and top views, we can see that the generated Ti layer has a porous structure.

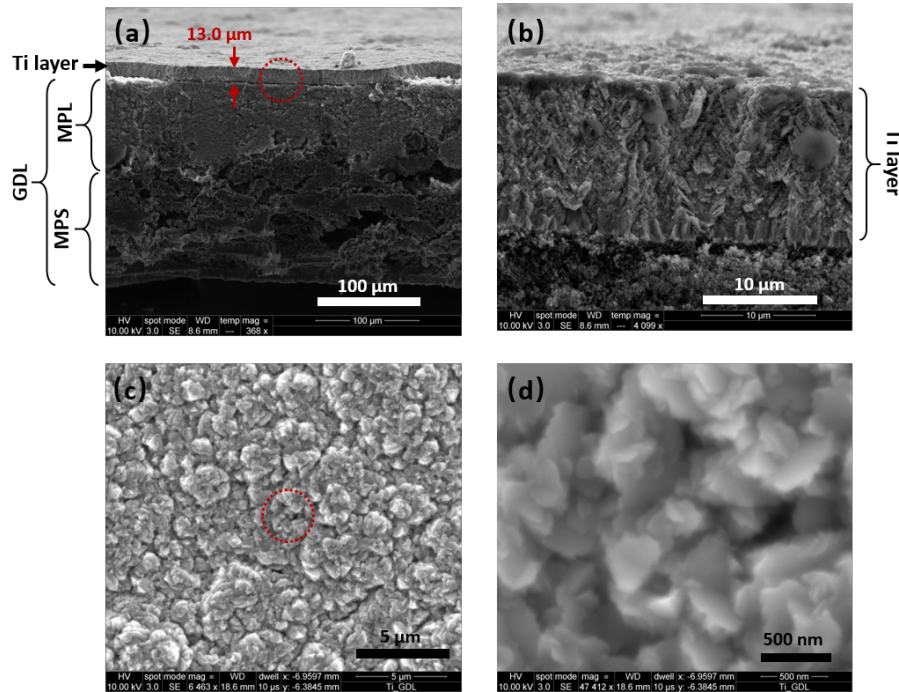


Figure 6.5: SEM images of (a) side view of the GDL and the sputtered 13.0 μm Ti protection layer. (b) Zoomed-in side view of the 13.0 μm Ti protection layer. (c) Top view of the 13.0 μm Ti protection layer. (d) Zoomed-in top view of the 13.0 μm Ti protection layer.

Figure 6.6 shows the cell voltage change during repeated hydrogen starvation tests. Figure 6.6a is the cell voltage change for the MEA with Pt black + 4.8 μm Ti layer anode.

Unlike the previous MEAs with either Pt/C anode or Pt black-only anode, for the MEA with Pt black + Ti layer anode, the cell voltage stayed at around -2.0 V for 55 min during the hydrogen starvation test without dropping to the cutoff voltage limit of -2.5 V. This suggests a very stable OER reaction for the anode during hydrogen starvation. Figure 6.6b is the cell voltage change for the MEA with Pt black + 13.0 μm Ti layer anode. Similarly, we can see that the cell stayed at -2.0 V during the testing period. The only difference is that, for the anode with 13.0 μm -thick Ti layer, cell voltage plots almost overlapped with each other during repeated hydrogen starvation tests, whereas there is a consecutive voltage decrease of around 24 mV in the stabilized cell voltage after each round of hydrogen starvation test for the anode with 4.8 μm -thick Ti layer. This slight voltage decrease is likely to be caused by accumulated cell performance degradation, which will be discussed in the following section.

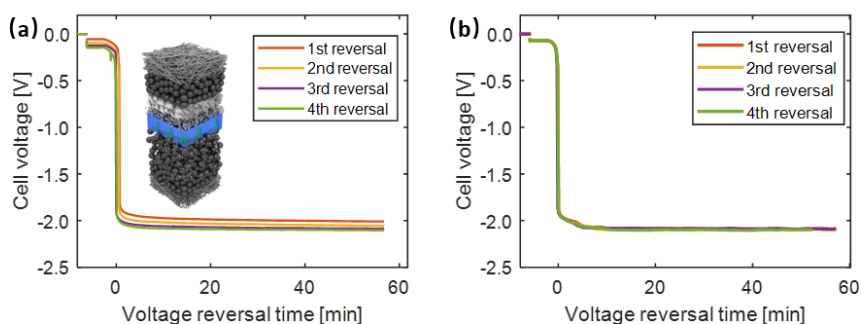


Figure 6.6: Cell voltage change during hydrogen starvation test for (a) MEA with Pt black + 4.8 μm Ti layer anode and (b) MEA with Pt black + 13.0 μm Ti layer anode

Figure 6.7 shows the electrochemical characterization results of the MEAs with Pt black and Ti layer anodes after hydrogen starvation tests. Figure 6.7a-1 shows CV curves of the MEA with Pt black + 4.8 μm Ti layer anode. Compared with the initial BOL CV curve, after the hydrogen starvation test, there is a noticeable increase in the magnitude of HQ-Q peaks, indicating a certain amount of carbon corrosion at the anode. In contrast,

Figure 6.7a-2 shows CV curves of the MEA with Pt black + 13.0 μm Ti layer. It is observed that the magnitude of HQ-Q peaks in the anode CVs of the MEA with Pt black + 13.0 μm Ti layer increases negligibly with the magnitude of the peaks being much smaller than that of the MEA with Pt black + 4.8 μm Ti layer anode. Also, the hydrogen adsorption/desorption peaks from 0.0 V to 0.3 V overlap with each other, suggesting a negligible change in the anode electrochemical active surface area (ECSA). Figure 6.7b-1 shows the EIS Nyquist plot for the MEA with Pt black + 4.8 μm Ti layer anode. From the plot, we see a slight increase in the HFR as well as the charge transfer resistance upon repetitive reversal tests. In contrast, as shown in Figure 6.7b-2, the EIS results of the MEA with Pt black + 13.0 μm Ti layer exhibit substantially no increase in HFR and very slight increase in the charge transfer resistance. Figure 6.7c-1 presents polarization curves for the MEA with Pt black + 4.8 μm Ti layer anode. We see a gradual decrease in the cell performance after the repetitive reversal tests. It should be noted that Figure 6.7c-1 exhibits the degradation of the MEA with Pt black + 4.8 μm Ti layer anode after nearly three hours of the cell in hydrogen starvation and cell reversal state. Compared with the MEA with Pt/C anode and that with Pt black-only anode samples, the degradation rate of the MEA with Pt black + 4.8 μm Ti layer anode is much slower. As mentioned previously, it is likely that this slow anode degradation results in the slow decrease in the cell voltage during the hydrogen starvation test. Figure 6.7c-2 shows the polarization curves of the MEA with Pt black + 13.0 μm Ti layer. From the polarization curves, we can see that there is much less cell performance degradation even after the longest duration of approximately four hours of the cell under hydrogen starvation and cell reversal state.

Figure 6.8 shows the comparison of degradation rates of MEAs with different anode structures. The y-axis values represent the normalized cell voltages obtained from polarization curves for different MEAs at 0.4 A/cm², and the x-axis values indicate the accumulated voltage reversal time, which is the sum of each cell reversal time that the cell

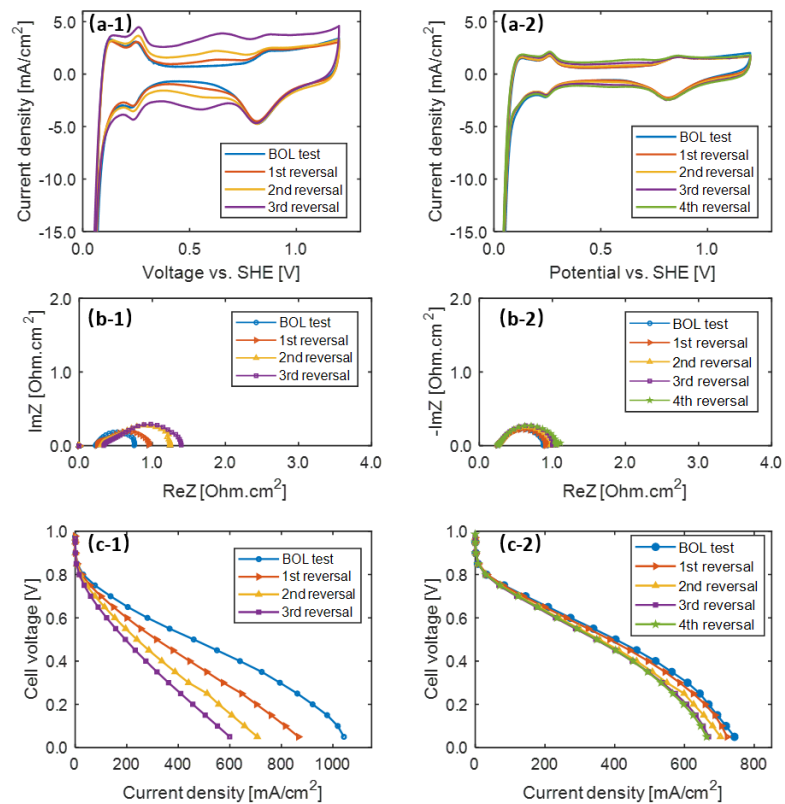


Figure 6.7: Post-characterization results of MEAs with Pt black and Ti layer anodes after hydrogen starvation tests. Anode CV curves for MEAs with Pt black + 4.8 μm (a-1) and 13.0 μm (a-2) Ti layer anodes. EIS Nyquist plots at 0.5 V for MEAs with Pt black + 4.8 μm (b-1) and 13.0 μm (b-2) Ti layer anodes. Polarization curves for MEAs with Pt black + 4.8 μm (c-1) and 13.0 μm (c-2) Ti layer anodes.

has been tested. The data of MEAs with 5 wt% and 50 wt% IrO₂ anodes were reproduced from the work by Mandal *et al.* [5]. From the plot, we can see that the MEA with Pt/C anode exhibits the highest voltage degradation rate of 15.2 %/min and thus the lowest reversal tolerance. The MEA with Pt black-only anode has a higher voltage degradation rate of 3.6 %/min and a slightly higher reversal tolerance. As for the MEA with anode Ti protection layers, we can see that the MEA with Pt black + 4.8 μm Ti anode has a relatively low voltage degradation rate of 0.29 %/min, and the reversal tolerance is comparable to that of the MEA with 50 wt% IrO₂ anode. Interestingly, the MEA with Pt black + 13.0 μm Ti anode has the lowest voltage degradation rate of 0.045 %/min and the highest reversal tolerance, whose durability is approximately 340-fold higher than that of the benchmark MEA with Pt/C anode.

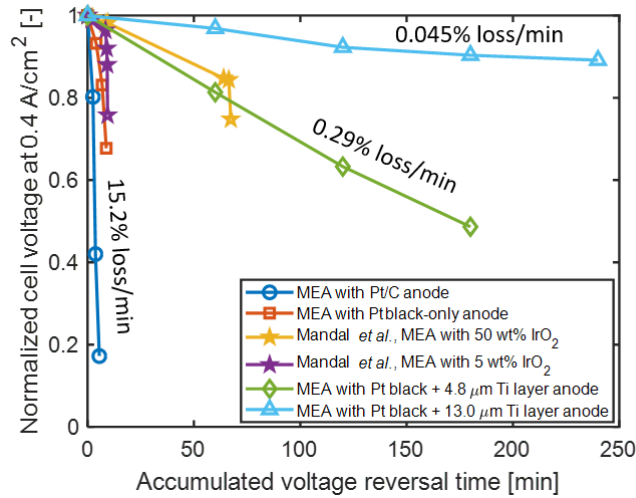


Figure 6.8: Normalized cell voltage at 0.4 A/cm² vs. accumulated voltage reversal time. The data of MEAs with 5 wt% and 50 wt% IrO₂ anodes were reproduced from the work by Mandal *et al.* [5]

6.4 Conclusions

In this chapter, we examined the hydrogen starvation damage to MEAs with different anode structures. The MEA with Pt/C anode exhibits the lowest reversal tolerance. The cell failed in a short time, and significant cell performance degradation was observed. As for the MEA with Pt black-only anode, though there is no carbon present in the anode, there is no significant improvement in the reversal tolerance. The cell still failed very quickly in the hydrogen starvation condition. The degradation pattern is different from that of the benchmark MEA with Pt/C anode, and the electrochemical characterization results suggest the carbon corrosion of MPL in the GDL. By adding Ti protection layer between catalytic Pt black layer and the MPL in the GDL, we observed a significant improvement in the anode reversal tolerance. The MEA with Pt black + Ti layer anode lasted for several hours in the hydrogen starvation stage without cell failure. The cell reversal tolerance of the MEA with Pt black + 13.0 μm Ti layer anode is approximately 340-fold higher than that of the benchmark MEA with Pt/C anode. These findings will greatly contribute to designing a new concept of RIAs and enhancing the cell voltage reversal tolerance of PEMFCs dramatically under severe operating conditions of hydrogen starvation and thus perfecting the competitiveness of FCEVs.

Chapter 7

Selective Anode and Its Application in Preventing Start-up/shutdown Damage

7.1 Introduction

This chapter presents the study of the effect of selective anode to the mitigation of the start-up/shutdown damage. Start-up/shutdown (SUSD) damage is a degradation mechanism that happens during the start-up or shutdown process of the fuel cell system. During SUSD, the anode hydrogen will be replaced by air or the existing air will be replaced by hydrogen. This process will create a temporary air/hydrogen gas boundary at the anode, which will alter the electrolyte potential distribution inside the cell. One significant effect is that, as the electrolyte potential changes, at certain point, the interfacial potential difference between the electrolyte and the cathode electrode increases, and carbon corrosion occurs. SUSD damage is slower compared with previously discussed hydrogen starvation damage, but it still has a large impact on the fuel cell system durability. The SUSD damage mainly results from the change of electrolyte potential distribution caused by the anode hydrogen/air gas boundary. One solution is to replace the anode platinum (Pt) catalyst with some other catalyst that has high hydrogen oxidation reaction (HOR) activity

but low oxygen reduction reaction (ORR) activity. In this chapter, we explored different alloy composition between Pt and iridium (Ir). The purpose is to find the optimum composition for the anode that can enhance the SUSD durability without sacrificing the fuel cell performance. We simulate the SUSD process by constantly altering the anode gas from hydrogen to air and from air to hydrogen. After examining a wide variety of catalyst combinations, we find that the anode catalyst that provides the best SUSD durability is the Ir catalyst. All the alloy catalyst like Ir₃Pt₁, Ir₁Pt₁ and Ir₁Pt₃ are not comparable to the Ir catalyst in terms of SUSD durability. From the cyclic voltammetry (CV) characterizations, we find that the Pt and Ir alloy anode catalyst are not as stable as the Ir or Pt catalyst after repeated SUSD cycles.

7.2 Experimental

Figure 7.1a shows the current design of the experiment setup. Initially, we plan to use a solenoid valve to control the on and off of the hydrogen and air gas flow to the anode. However, a trial test showed that the solenoid valve will cause gas pressure build up and lead to a sudden high flow rate purge to the anode, which is very different from the desired formation of uniform hydrogen/air gas boundary. So, in later experiment setup we removed the solenoid valves, and the gas flow rate of the hydrogen and air to the cathode were controlled by the Scribner software. For the cathode, we used a separate humidifier tank. To prevent the mixing of air with residual hydrogen or vice versa, one-way valves were used for the air and hydrogen inlet to the anode, as shown in Figure 7.1b. Figure 7.1c shows the connection of the extra humidifier to the cathode side.

During the start-up/shutdown gas purging cycles, the cell temperature is set to be 65 °C. The anode hydrogen and air gas flow rates are set to be 100 ml/min. The dew points of the hydrogen and air humidifiers are 65 °C to achieve 100 % relative humidity. The

Table 7.1: Experiment parameters for the electrochemical characterizations

Test type	Conditioning	CV	IV	EIS
Active area [cm ²]	5	5	5	5
Cell temperature [°C]	65	65	65	65
Gas type (An/Ca)	H ₂ /Air	H ₂ /N ₂	H ₂ /Air	H ₂ /Air
Gas flow rates (An/Ca) [ml/min, lm/min]	200/550	200/200	200/550	200/550
Dew point (An/Ca) [°C, 1°C]	65/65	65/65	65/65	65/65
Current density range [A/cm ²]	0.05-1		So that potential above 0.3V	0.1 and 0.4
Potential range [V]		0.04-1.2		
Scan rate [mV/s]		50		
AC amplitude				5% of DC current
Frequency range [Hz]				0.1-100 kHz

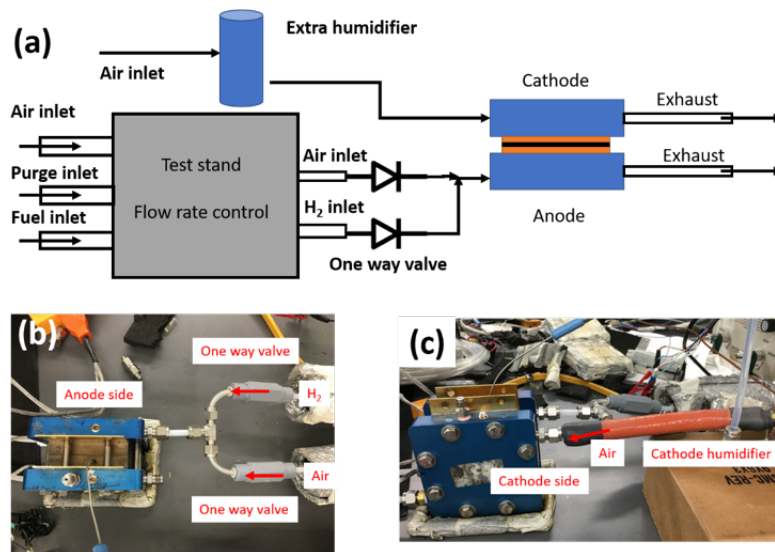


Figure 7.1: (a) Experiment setup for the start-up/shutdown test; (b) Gas tube connection of the anode side; (c) Connection of the extra gas humidifier to the cathode side.

air supplied to the cathode is also 65 °C and 100% relative humidity (RH). For the start-up/shutdown tests, the anode gas is switched for every 30 s. It should be noted that the initial test for carbon supported Pt catalyst (Pt/C) anode is 1 min.

Figure 7.3 shows the experimental procedure of the start-up/shutdown tests. Firstly, the assembled testing cell will be conditioned at 65 °C, 100% RH and hydrogen/air environment for 8 hrs. Then the initial beginning of life (BOL) polarization curve, CV curves, and electrochemical impedance spectroscopy (EIS) will be measured. Once that is done, the cell will experience start-up/shutdown cycles with cycle numbers of 100, 200, 400 and 400 till 1100 cycles is reached. After each cycling tests, the electrochemical characterization will be conducted. The characterization parameters are listed in Table 7.1. It should be noted that, for the Pt/C anode sample, the cell geometric area is 4 cm² and for the other cells the geometric area is 5 cm².

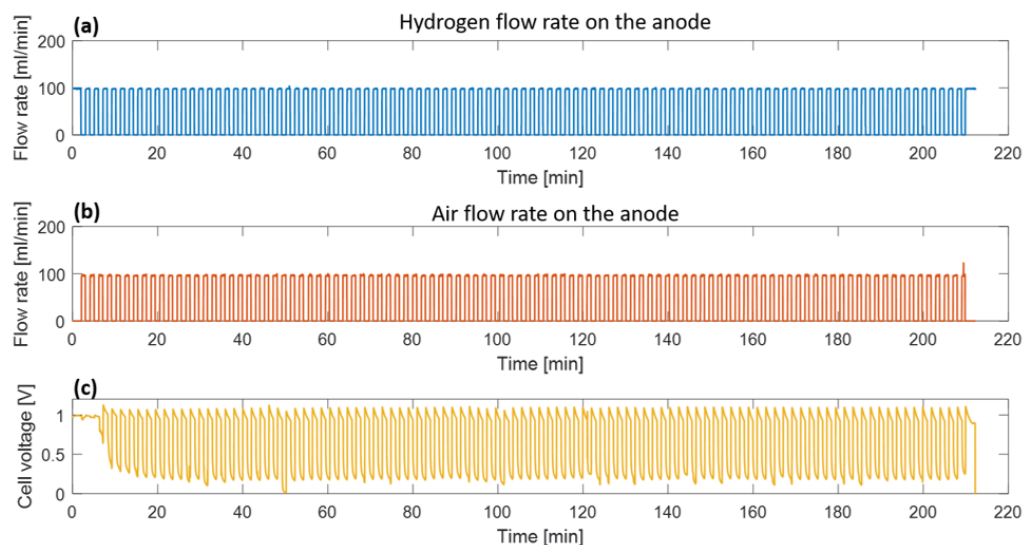


Figure 7.2: Start-up/shutdown cycles. (a) The hydrogen flow rate vs. time and (b) the cathode flow rate vs. time. (c) The cell voltage change vs. time.

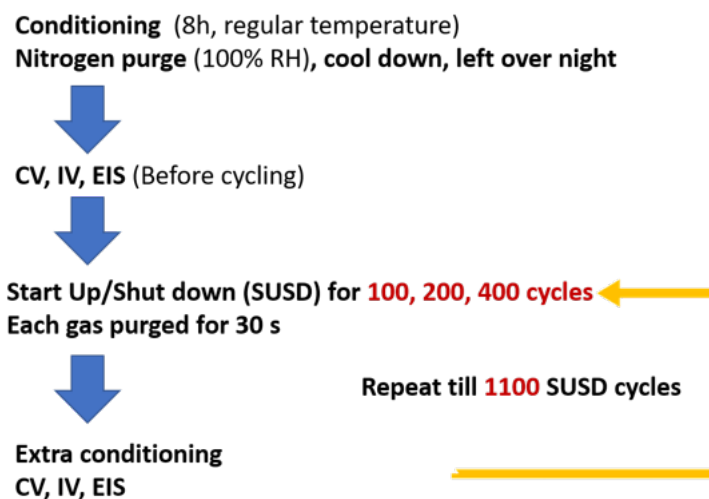


Figure 7.3: The experiment procedure of the start-up/shutdown test.

7.3 Results and discussion

7.3.1 SUSD test results of the Pt/C sample

Figure 7.4 and Figure 7.5 show the characterization of the catalyst coated membrane (CCM) sample with Pt/C anode at the BOL state and after each start-up/shutdown cycle. From the polarization curve, we can see that the performance decreases as the start-up/shutdown cycle number increases. From the cathode CV curves, we can see that the peak current for both hydrogen adsorption/desorption and platinum oxide formation /reduction keep decreasing as the cycle number increases. However, no significant peak at around 0.5-0.7 V due to the hydroquinone-quinone (HQ-Q) redox reaction could be observed. But at the same time, the continuous decrease in the electrical double layer (EDL) current density at potential window 0.3 - 0.5 V from the cathode CV still suggest certain extent of carbon surface loss. As for the anode CV, we can see that there is a slight crease of hydrogen adsorption/desorption peaks, but not as significant as the cathode. From the EIS results, we can see that both the high frequency resistance (HFR) and the cathode charge transfer resistance are increasing as the start-up/shutdown test continues.

7.3.2 SUSD test results of the Pt₁Ir₁/C sample

Figure 7.6 and Figure 7.7 show the characterization of the CCM sample with Pt₁Ir₁/C anode at the BOL state and after each start-up/shutdown cycle. Similar to the Pt/C anode CCM sample, the current density keeps decreasing from the polarization curves. From the cathode CV curves, we can see that the cell active surface area keeps decreasing as the cycle number increases, however, the initial loss is not as big as the Pt/C anode CCM sample. The anode CV shape is very different from the typical Pt/C CV curve. The deformed shape could be the result of the alloy effect and the presence of Ir at the anode.

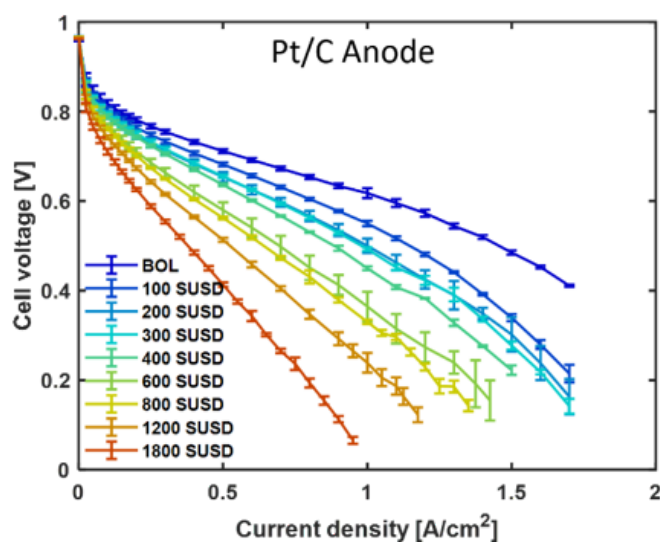


Figure 7.4: Polarization of the CCM with Pt/C anode of the BOL state and after each start-up/shutdown cycling test.

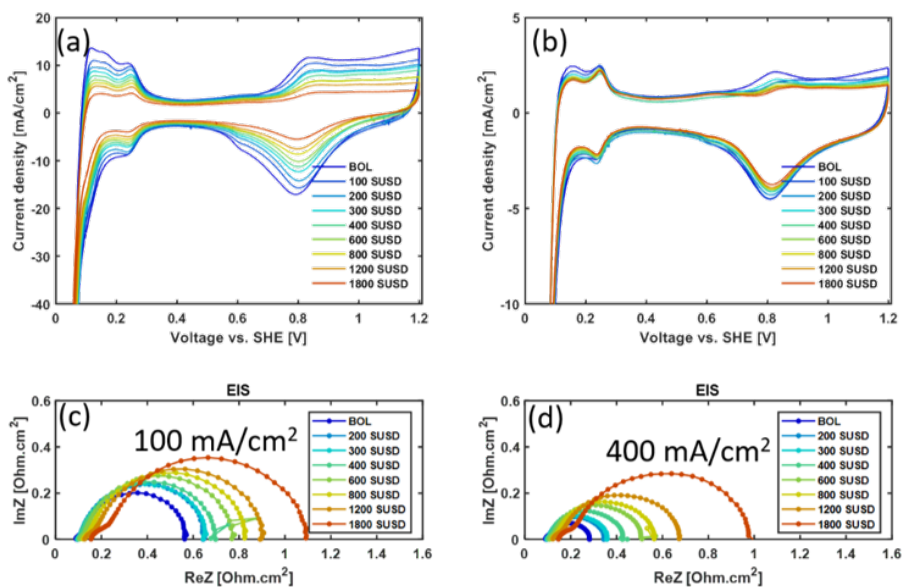


Figure 7.5: (a) CV curves of the cathode. (b) CV curves of the anode. (c) Nyquist plots at 100 mA/cm². (d) Nyquist plots at 400 mA/cm².

Different from the anode CV of the Pt/C sample, the $\text{Pt}_1\text{Ir}_1/\text{C}$ anode CV shows a much significant active surface area loss. From the EIS results, there is less increase in the HFR and the charge transfer resistance compared with the Pt/C anode sample.

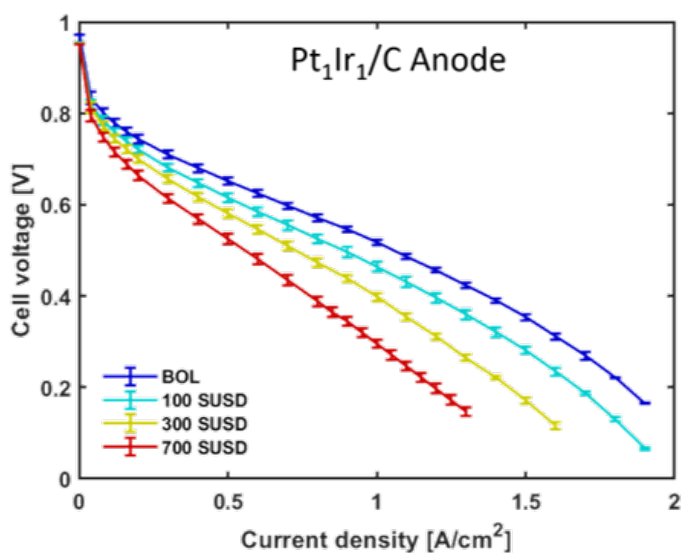


Figure 7.6: Polarization of the CCM with $\text{Pt}_1\text{Ir}_1/\text{C}$ anode of the BOL state and after each start-up/shutdown cycling test.

7.3.3 SUS test results of the $\text{Pt}_3\text{Ir}_1/\text{C}$ sample

Figure 7.8 and Figure 7.9 show the characterization of the CCM sample with $\text{Pt}_3\text{Ir}_1/\text{C}$ anode at the BOL state and after each start-up/shutdown cycle. From the polarization curves, there is less degradation of the $\text{Pt}_3\text{Ir}_1/\text{C}$ sample during the initial 100 start-up/shutdown cycles compared with the $\text{Pt}_1\text{Ir}_1/\text{C}$ sample. The comparison of the current densities of different samples at 0.7 V will be discussed later in Figure 7.12. As for the cathode CV, we see a similar pattern of active surface area decrease. However, different from the Pt/C anode sample, the $\text{Pt}_1\text{Ir}_1/\text{C}$ and $\text{Pt}_3\text{Ir}_1/\text{C}$ anode samples' cathode CV show no significant decrease of the EDL current density. From the EIS results, the HFR and charge transfer resistance increase is less significant compared with the $\text{Pt}_1\text{Ir}_1/\text{C}$ anode sample after the

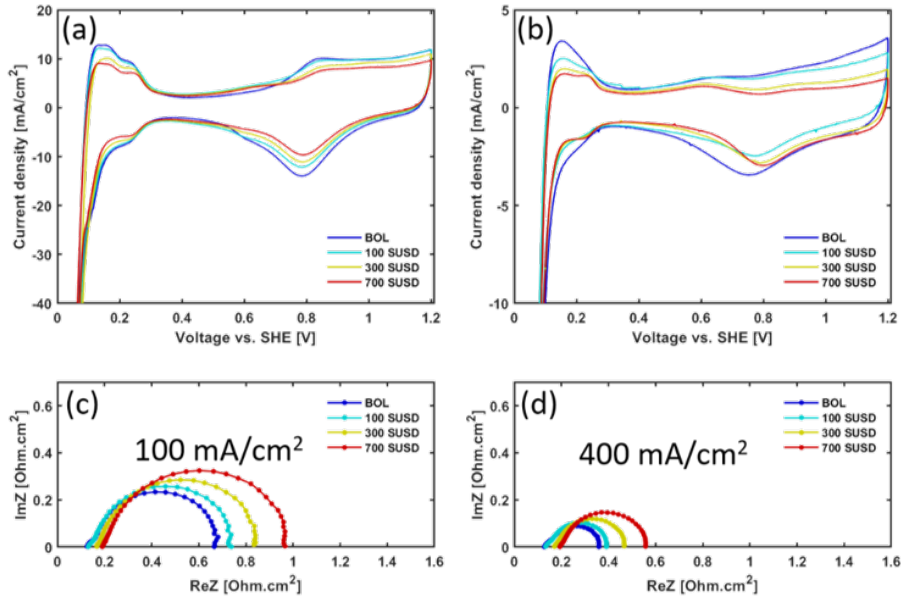


Figure 7.7: (a) CV curves of the cathode. (b) CV curves of the anode. (c) Nyquist plots at 100 mA/cm². (d) Nyquist plots at 400 mA/cm².

same cycle numbers.

7.3.4 SUSD test results of the Pt₁Ir₃/C sample

Figure 7.10 and Figure 7.11 show the characterization of the CCM sample with Pt₁Ir₃/C anode at the BOL state and after each start-up/shutdown cycle. Different from the Pt₃Ir₁/C sample, the decrease of the cell performance is faster after the initial start-up/shutdown cycles and tends to slow down later on, based on the polarization results. From the cathode CV curves, we see less decrease in the active surface area compared with Pt₃Ir₁/C sample and Pt₁Ir₁/C sample. After the first 100 start-up/shutdown cycles, there is a slight increase in the EDL current density. The EDL current density stabilized for the rest of the cycling tests. As for the anode, there is a significant decrease in active surface area for the first 100 and 300 start-up/shutdown cycles. For the EIS results, the increase in the HFR is less significant compared with Pt₁Ir₁/C sample and the Pt₃Ir₁/C sample. Also, the in-

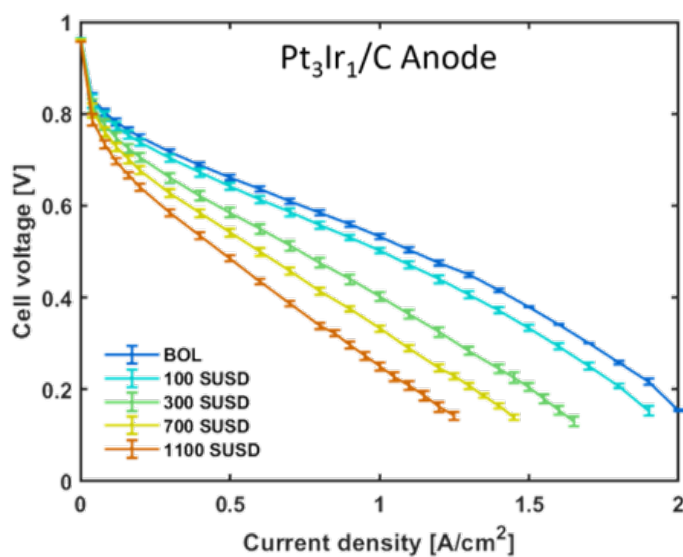


Figure 7.8: Polarization of the CCM with $\text{Pt}_3\text{Ir}_1/\text{C}$ anode of the BOL state and after each start-up/shutdown cycling test

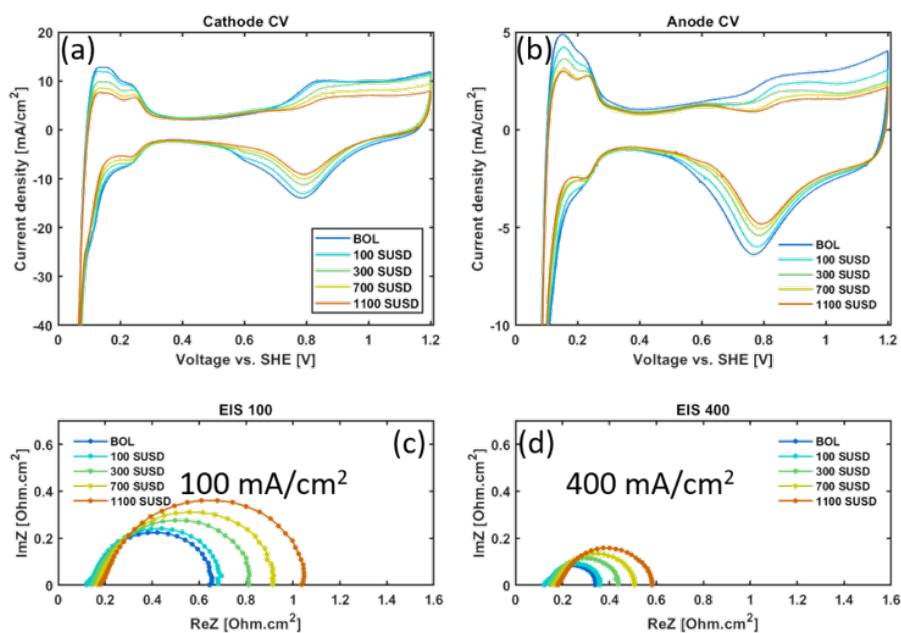


Figure 7.9: (a) CV curves of the cathode. (b) CV curves of the anode. (c) Nyquist plots at 100 mA/cm^2 . (d) Nyquist plots at 400 mA/cm^2 .

crease of the charge transfer resistance tends to slow down as the start-up/shutdown cycles increase, which corresponds well with the decreasing trend of the polarization curves.

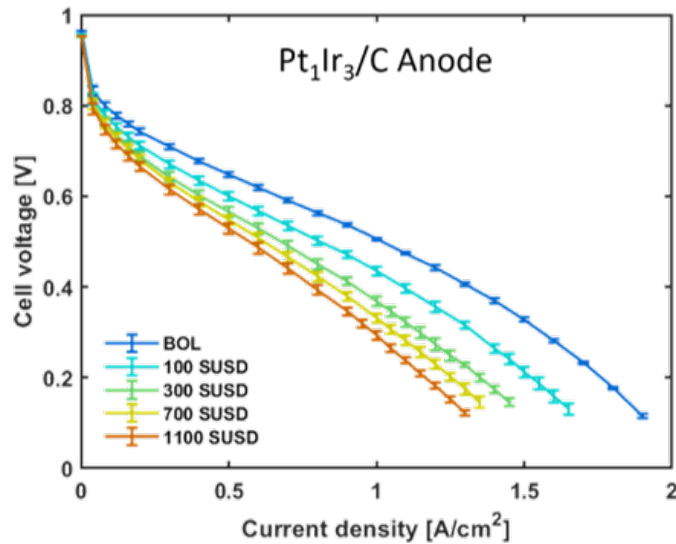


Figure 7.10: Polarization of the CCM with $\text{Pt}_1\text{Ir}_3/\text{C}$ anode of the BOL state and after each start-up/shutdown cycling test.

7.3.5 Comparison of the ECSA and current density change

The cathode electrochemical active surface area (ECSA) was calculated by integrating the charge of the hydrogen desorption peak with EDL current density subtracted, and converted to the surface area with a reference charge density value of $0.21 \text{ mC}/\text{cm}_{\text{Pt}}^2$. For better comparison, the ECSA are then normalized based on the BOL ECSA, and the comparison is shown in Figure 7.12a. For all these four samples, the normalized ECSA decreased rapidly during the initial start-up/shutdown cycles. The decreasing trends all start to slow down after about 300 cycles. Among the samples, the Pt/C anode sample has the largest overall ECSA decreasing rate, while in comparison, the $\text{Pt}_1\text{Ir}_3/\text{C}$ anode sample has the slowest ECSA decreasing rate. Figure 7.12b shows the normalized cell current density at 0.7 V. However, the normalized sample current densities do not follow

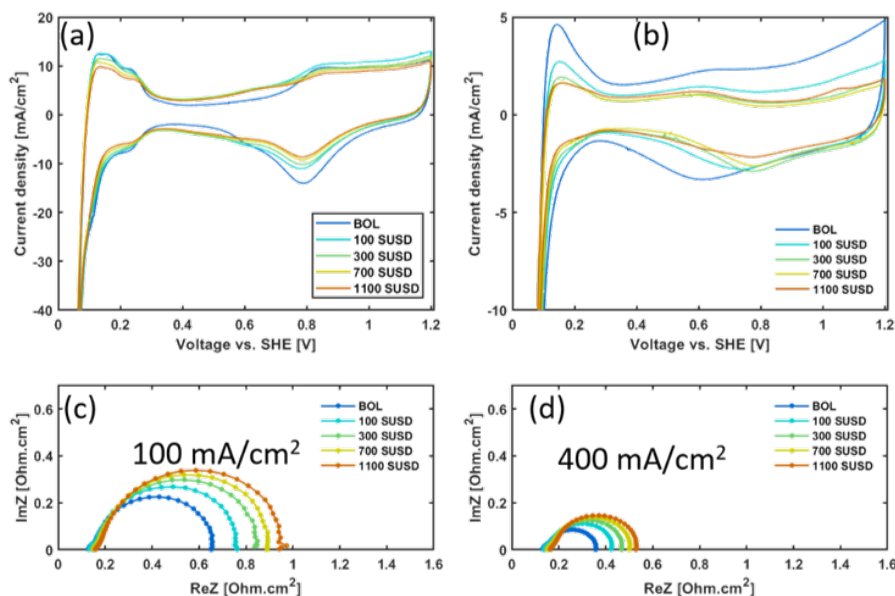


Figure 7.11: (a) CV curves of the cathode. (b) CV curves of the anode. (c) Nyquist plots at 100 mA/cm². (d) Nyquist plots at 400 mA/cm².

the same trend as the ECSA decrease. The cause of this discrepancy requires further study of the individual losses in the cell.

7.3.6 Anode potential change during startup/shutdown with reference electrode

With reference electrode, we can measure individual electrode potential change during the startup/shutdown tests. As shown in Figure 7.13, during the startup/shutdown tests, the cell voltage cycles between 1.1 V and 0.3 V as the anode gas environment changes. The low cell voltage is related to the anode in air environment and the high cell voltage is related to the anode in hydrogen environment. As for the anode potential measured from the reference electrode, we can see that when there is hydrogen, the anode potential is near 0 V and when there is air, the anode potential goes up to about 0.95 V. The high cathode potential happens at the beginning of the anode gas switches from hydrogen to air.

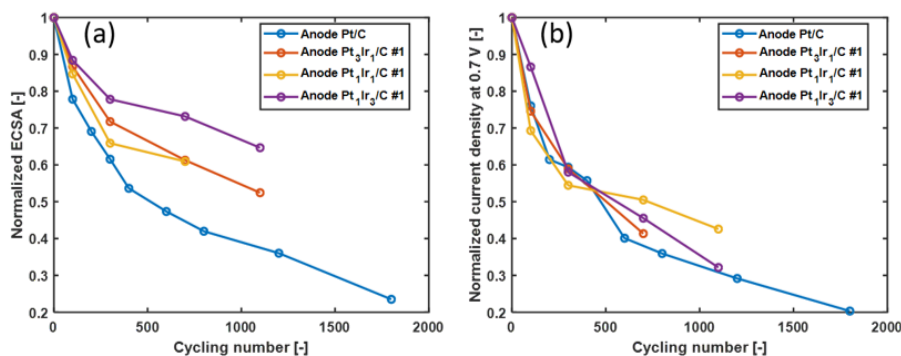


Figure 7.12: Comparison of samples with different anode catalyst of the (a) Normalized electrochemical active surface area. (b) Normalized current density at 0.7 V.

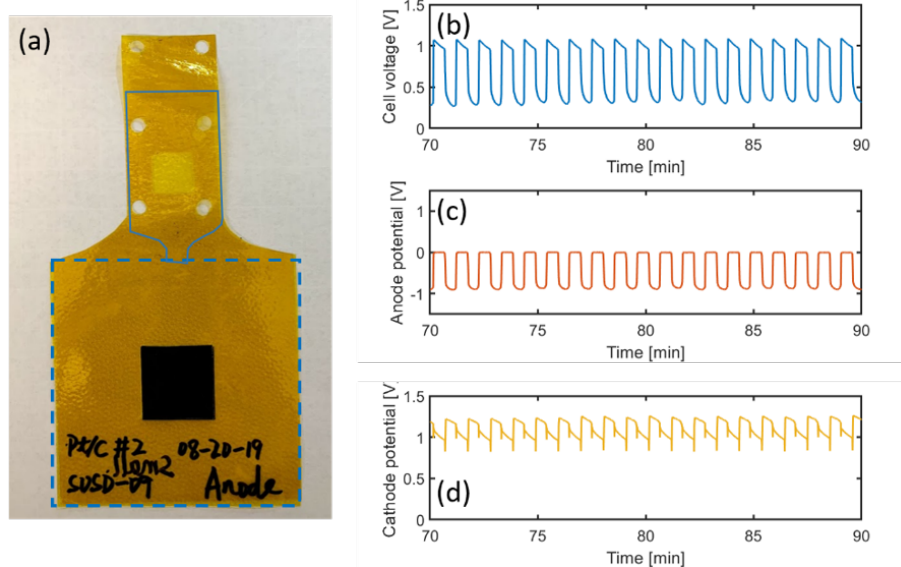


Figure 7.13: (a) Picture of the reference electrode and its integration into the MEA. (b) The cell voltage change during startup/shutdown tests. (c) Anode potential change during the startup/shutdown tests. (d) Cathode potential change during the startup/shutdown tests.

7.4 Conclusions

In this study, we examined different selective anode catalysts and their effect to the fuel cell SUSD durability. The SUSD cycle is done by alternating the anode gas from hydrogen to air and from air to hydrogen. Based on the reference electrode test, we can see that this alternating gas environment can actually cause the interfacial potential difference at the cathode to increase. Based on the electrochemical characterizations after SUSD tests of different anode catalyst materials, we find that the anode catalyst that has the best SUSD durability is the ir catalyst. As for Pt and Ir alloy catalyst with different compositions, though they all show better SUSD durability compared with the conventional Pt/C catalyst, from anode CV curve measurements, they all show certain extend of stability issue, as some characteristic peaks at the BOL state were disappeared or shifted as the SUSD test continues. The change in anode CV curves suggests a degradation of these alloy anode catalysts. Transmission electron microscope (TEM) and X-ray scattering might be helpful to characterize the change in the catalyst nanoparticles after SUSD cycles.

Chapter 8

Conclusion, Contributions and Future Work

8.1 Conclusions and contributions

8.1.1 Proton Transport at Metal/Water Interfaces

This chapter presented the study on proton transport properties at metal/water interfaces. Two types of metal surfaces were studied, gold (Au) surface and platinum (Pt) surface. The Pt surface is studied because it is the commonly used catalyst material for fuel cell systems. However, there are some complications on Pt surface within the voltage window of different studies, like the hydrogen adsorption and desorption at low electrode potentials. and oxide formation and reduction at high electrode potentials. The Au is introduced as a model surface because negligible surface reactions at the voltage window during cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies. We firstly examined the water dependence of each electrode's electrochemically active roughness factor (ECRF) by measuring the CV curves at different relative humidity (RH)s. We found that for both the Pt and Au electrode, the ECRF increases with RH, suggesting that the ion accessible (i.e., electrochemically active) metal surface during CV measure-

ments is dependent on water. We then tested each electrode's oxygen reduction reaction (ORR) activity, and we found that the ORR current followed the same trend as the ECRF. These findings are indicating that the proton transport in these ionomer-free electrode is highly dependent on water. We then used micro-structured electrode scaffold (MES) device and current interrupt method to test each electrode's ionic conductivity at different electrode potential. What we found is that, for both Pt and Au ionomer-free electrodes, their ionic conductivity is highly dependent on the water content inside each electrode, corresponds very well with CV and polarization curve measurements. As for the potential dependence, we found that the Au ionomer-free electrode shows an typical electrical double layer (EDL) behavior, where the ionic conductivity value is the lowest near the potential of zero charge (PZC). However, for the Pt electrode, its ionic conductivity show no significant potential dependence. We think the surface hydrogen adsorption/desorption at low electrode potentials, and the surface oxide formation/reduction might be the reason that altered the charge density at the Pt/water interface.

8.1.2 Proton Transport at Carbon/Water Interfaces

This chapter presented the proton transport properties at carbon/water interfaces. The proton transport properties at the carbon/water interfaces is critical to the understanding of the Pt utilization of conventional carbon supported Pt catalyst (Pt/C) catalyst layer. We used EIS measurement and transmission line model to get the proton transport properties of a porous electrode made of Vulcan XC-72R carbon black, a commonly used carbon support material, for this study. We examined the ionic conductivity's potential dependence and RH dependence. Interestingly, in the potential range that we tested (0.0 - 1.0 V), the ionic conductivity of the carbon porous electrode decreased monotonically with the electrode's potential. The electrode's ionic conductivity also showed a strong dependence on water, as the RH increased, the ionic conductivity also increased. We also examined the presence

of Pt nanoparticles to the ionomer-free electrode's ionic conductivity, by conducting the same EIS test on 10 wt% Pt/C catalyst layer. The ionic conductivity of this 10 wt% Pt/C ionomer-free electrode show no significant difference from the Vulcan carbon electrode, suggesting that the ionic conductivity throughout the electrode is dominated by the continuous carbon surface. The observed potential dependence of the carbon/water interface is supported by separate CV measurements. From the measured CV curves, the electrical double layer capacitance is high at low potentials and low at high potentials. This finding indicates that there is limited amount of carbon surface is accessible to ions at high potentials, corresponds well with the ionic conductivity values measured at different electrode potentials by EIS.

8.1.3 Hydrogen Starvation at High Temperatures and Reversal Tolerant Catalyst Failure Mechanism

This chapter examined the water electrolysis catalyst failure mechanism under hydrogen starvation conditions. It has been reported that the reversal tolerant anode (RTA) can prolong water electrolysis reaction against carbon corrosion reaction, because of the extra amount of oxygen evolution reaction (OER) catalyst it contains. However, it is found that the OER catalyst can only sustain the water electrolysis reaction for a certain period of time before it become deactivated. The water electrolysis time that the extra amount of OER catalyst can sustain is also dependent on the electrode's RH. It is counter intuitive that at the OER catalyst at fully humidified conditions performed as bad at dry conditions. In this study, we used a self-designed water electrolysis cell to study the deactivation mechanism of the commonly used OER catalyst, iridium oxide (IrO_2). We tested the activity of the IrO_2 catalyst at different RH conditions and compared it with the tested activity of carbon corrosion reaction (COR). We found that the catalytic activity of IrO_2

measured by the current density response shows a linear dependence on OER, while the rate of carbon corrosion increases exponentially with RH. This linear versus exponential relationship suggests that the higher rate of catalyst poisoning at high OERs is related to the exponentially increased rate of carbon corrosion, resulting in the impaired durability of RTAs.

8.1.4 Investigation of Hydrogen Starvation in Subfreezing Conditions

This chapter presented the study on hydrogen starvation in subfreezing conditions. Understanding hydrogen starvation and its potential damage to fuel cell system in subfreezing conditions is critical to the commercialization of fuel cell electric vehicles (FCEVs). At high temperatures, it is known that when there is not enough hydrogen supplied to the anode, the anode will experience a short period of water electrolysis reaction followed by carbon corrosion reaction. Adding OER catalyst will promote the water electrolysis reaction over carbon corrosion reaction. However, it is unclear if it is the same in subfreezing conditions. Our initial tests of hydrogen starvation in subfreezing condition showed that the cell voltage has a very different transient behavior compared with high temperature hydrogen starvation tests. We developed a hydrogen reference electrode that can operate in freezing conditions. With the reference electrode, we found that most of the cell voltage changes during hydrogen starvation tests in freezing conditions are not related to the anode potential change. During subfreezing cell reversal, we observed a single water electrolysis anode potential plateau, but the typically subsequent voltage plateau for carbon corrosion usually seen at high temperatures was not found. Repeated cell reversal tests at subfreezing temperature shows a much slower degradation rate compared with high temperature reversals. A series of isothermal reversal tests at different temperatures indicate that the degradation rate related with carbon corrosion is temperature dependent. As for the effect of RTA on the cell reversal behavior, we found at subfreezing temperatures that

the voltage reversal duration time of the membrane electrode assembly (MEA) with RTA is similar to that of the MEA without RTA. However, once the cell temperature was sufficiently above freezing, such as during the heating of the startup process, the MEA with RTA would facilitate water electrolysis reactions by consuming water and delaying the onset of carbon corrosion. Thus, our results show that cell reversal with subfreezing internal temperatures does not substantially degrade the anode by carbon corrosion, but that as the cell warms an RTA is one approach to extend the survival of the fuel cell stack.

8.1.5 Understanding Cell Reversal Damage: Towards Reversal Tolerant Anode

This chapter presented the works on the development of the reversal invincible anode (RIA). As discussed in previous sections, hydrogen starvation will cause the cell voltage reverse and carbon corrosion reaction, which will lead to significant degradation in cell performance and decrease in cell life time. Though it is shown that adding extra amount of OER catalyst to the anode can prolong the water electrolysis reaction, but the trace amount of carbon corrosion reaction will eventually deactivate the OER catalyst and lead to cell failure. A more robust approach to prevent hydrogen starvation induced damage will be beneficial to the fuel cell system's durability. We explored different anode configurations in order to find the best hydrogen starvation and cell reversal tolerant anode. For an MEA with conventional anode composed of Pt/C, the degradation caused by cell reversal primarily comes from the carbon support corrosion. It is noteworthy that an MEA with Pt black-only anode without any carbons also fails during hydrogen starvation. It is postulated that cell failure and performance degradation of the MEA with Pt black-only anode are caused by the corrosion of carbon materials present at the anode microporous layer (MPL) in gas diffusion layers. Based on these findings, we propose RIAs composed

of both Pt black as a catalyst layer and thin titanium (Ti) as a protective layer. The conventional MEA with Pt anode exhibits the highest cell voltage degradation rate of 15.2% loss/min and the lowest reversal tolerance, whereas the RIA MEA with Pt black and 13.0 μm -thick Ti layer anode performs the lowest cell voltage degradation rate of 0.045% loss/min and the highest reversal tolerance which is approximately 340-fold increase compared with the conventional MEA with Pt/C anode. These findings will greatly contribute to designing a new concept of RIAs and enhancing the cell voltage reversal tolerance of polymer electrolyte membrane fuel cell (PEMFC)s dramatically under severe operating conditions of hydrogen starvation and thus perfecting the competitiveness of FCEVs.

8.1.6 Selective Anode and Its Effect in Preventing Start-up/shutdown Damage

This chapter presented the study of the effect of selective anode to the mitigation of the start-up/shutdown damage. Start-up/shutdown (SUSD) damage is a degradation mechanism that happens during the start-up or shutdown process of the fuel cell system. During SUSD, the anode hydrogen will be replaced by air or the existing air will be replaced by hydrogen. This process will create a temporary air/hydrogen gas boundary at the anode, which will alter the electrolyte potential distribution inside the cell. One significant effect is that, as the electrolyte potential changes, at certain point, the interfacial potential difference between the electrolyte and the cathode electrode increases, and carbon corrosion occurs. SUSD damage is slower compared with previously discussed hydrogen starvation damage, but it still has a large impact on the fuel cell system durability. The SUSD damage mainly results from the change of electrolyte potential distribution caused by the anode hydrogen/air gas boundary. One solution is to replace the anode Pt catalyst with some other catalyst that has high hydrogen oxidation reaction (HOR) activity but low ORR activity.

In this chapter, we explored different alloy composition between Pt and iridium (Ir). The purpose is to find the optimum composition for the anode that can enhance the SUSD durability without sacrificing the fuel cell performance. We simulate the SUSD process by constantly altering the anode gas from hydrogen to air and from air to hydrogen. After examining a wide variety of catalyst combinations, we find that the anode catalyst that provides the best SUSD durability is the Ir catalyst. All the alloy catalyst like Ir_3Pt_1 , Ir_1Pt_1 and Ir_1Pt_3 are not comparable to the Ir catalyst in terms of SUSD durability. From the CV characterizations, we find that the Pt and Ir alloy anode catalyst are not as stable as the Ir or Pt catalyst after repeated SUSD cycles.

8.2 Future Work

8.2.1 Diode Integrated MEA with High Cell Reversal Tolerance

In Chapter 6 we discussed the approach of creating a Ti protection layer between the anode MPL and the Pt black catalyst layer in order to increase the anode reversal tolerance. This configuration showed very good enhancement on the anode reversal tolerance. However, creating this kind of Ti protection layer is very expensive. Also, a support-less Pt black catalyst layer is not an effective way to utilize Pt. A cheaper way to resolve this problem is needed. For the conventional approach of adding extra amount of OER catalyst or the new approach of using more stable Pt black + Ti protection layer, the underlying reason is to maintain water electrolysis reaction, when there is not enough hydrogen supply, so that charge can still transfer through the membrane in the form of protons. Another approach that worth trying is to find another way to transfer charge when hydrogen supply is off, like using an electronic component to bypass the current. As shown in Figure 8.1a and b, for a regular fuel cell during normal operating conditions, HOR will happen at the

anode and ORR will happen at the cathode. The cathode has higher potential than the anode. When hydrogen starvation happens, the anode potential increases to above 2 V and OER and COR will happen at the anode, leading to anode catalyst layer damage. In comparison, in Figure 8.1c and d, if the fuel cell is connected to a diode, during normal operating conditions, the cathode has higher potential than the anode, and no current can pass through the diode. The normal operation will not be affected by the diode. However, as the hydrogen supply is cut off, and the anode potential increases, current can pass through the diode. In this case the anode potential remain low and much less damage could happen to the anode. Preliminary results are shown in Appendix C.

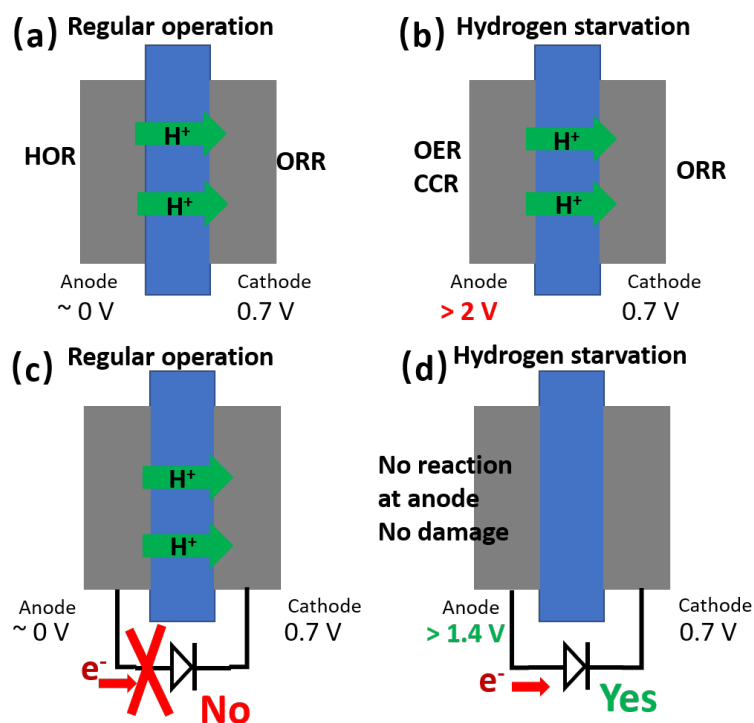


Figure 8.1: (a) Schematic of a regular fuel cell during normal operation. (b) A regular fuel cell under hydrogen starvation condition. (c) A fuel cell with diode during normal operating condition. (d) A fuel cell with diode during hydrogen starvation condition.

8.2.2 Examine the Contribution of Surface Functional Groups to the Ionic Conductivity of Carbon

As discussed in Chapter 3, the proton transport at carbon/water interfaces shows very interesting potential dependent behavior. As the electrode potential increases, the proton conductivity at the carbon/water interface decreases. The underlying mechanism is not so clear, and might be related to the surface potential-driven deprotonation process of carbon surface functional groups. To examine this hypothesis, it will be interesting to compare different carbon supports with modified or controlled types of surface functional groups and compare their ionic conductivity in the presence of water. After that, it will also be helpful to characterize the composition of surface functional groups of commonly used carbon supports. These information will provide useful guidance to the future catalyst support material design and optimization.

8.2.3 Temperature Monitoring During of Subfreezing Reversal Process

As discussed in Chapter 8, the carbon corrosion damage to the PEMFC anode is temperature dependent. From the anode potential change during hydrogen starvation, there is only OER in subfreezing temperature and the COR is suppressed. However, carbon corrosion damage to the cell will happen during the fuel cell system heating up process. During the hydrogen starvation test in Chapter 8, though the cell temperature is hold to be constant, the local temperature may be affected by trace amount of heat generated due to anode water electrolysis or cathode hydrogen evolution reaction (HER). Understanding how much the local temperature has changed during these hydrogen starvation test is very important. Also, a large portion of the isothermal hydrogen starvation tests in Chapter

8 are conducted using hydrogen pumping mode, with cathode supplied with nitrogen. It will be helpful if a comparison study of the local temperature change between hydrogen pumping mode experiment and experiments with the cathode supplied with air. Some of the preliminary results are shown in Appendix D

Appendix A

Abbreviations and Symbols

CO ₂	carbon dioxide.
Ir/C	carbon-supported Ir.
IrO ₂	iridium oxide.
IrRu ₄ /C	iridium ruthenium alloy with carbon support.
Ir	iridium.
APS	average particle size.
Au	gold.
BOL	beginning of life.
CCM	catalyst coated membrane.
COR	carbon corrosion reaction.
CV	cyclic voltammetry.
DOE	Department of Energy.
ECRF	electrochemically active roughness factor.
ECSA	electrochemical active surface area.
EDL	electrical double layer.
EDS	energy dispersive spectroscopy.

EIS	electrochemical impedance spectroscopy.
EOL	end of life.
FCEV	fuel cell electric vehicle.
FFT	fast Fourier transform.
FRT	first reversal time.
GDE	gas diffusion electrode.
GDL	gas diffusion layer.
H ₂	hydrogen.
HER	hydrogen evolution reaction.
HFR	high frequency resistance.
HOR	hydrogen oxidation reaction.
HRE	hydrogen reference electrode.
IPA	isopropanol.
MEA	membrane electrode assembly.
MES	micro-structured electrode scaffold.
MPL	microporous layer.
MPS	macro-porous substrate.
N ₂	nigrogen.
non-PGM	non-platinum group metal.
NSTF	nanostuctured thin film.
OCV	open circuit voltage.
OER	oxygen evolution reaction.
ORR	oxygen reduction reaction.

PCB	printed circuit board.
PEMFC	polymer electrolyte membrane fuel cell.
PFSA	perfluorosulfonic acid.
PGM	platinum group metal.
Pt	platinum.
Pt/C	carbon supported Pt catalyst.
PTFE	polytetrafluoroethylene.
PZC	potential of zero charge.
RE	reference electrode.
RH	relative humidity.
RHE	reversible hydrogen electrode.
RIA	reversal invincible anode.
RTA	reversal tolerant anode.
SEM	scanning electron microscope.
SHE	standard hydrogen electrode.
SUSD	start-up/shutdown.
TEM	transmission electron microscope.
Ti	titanium.

Appendix B

PFIB-SEM image segmentation

B.1 Segmentation based on fast Fourier transform method

As shown in Figure B.1 are different steps using fast Fourier transform (FFT) segmentation method. The original image is shown as Figure B.1-1. Firstly, the image was normalized so that it has a good contrast and a reasonably distributed histogram. By FFT transform and only threshold the high frequency region and transform back to the image form, we can get Figure B.1-3. Figure B.1-3 contains the basic edge information, but the image is still gray scale. Using simple threshold method, we can transform grayscale Figure B.1-3 to binary image as shown in Figure B.1-4. However, the binarization process sometimes will lead to a discontinuous edge. To solve that problem, we used a distance map to close the small gaps and generate continuous curves. The distance map is shown in Figure B.1-5, it is a new grayscale image, and the pixel intensity represents the distance of each pixel from the valid edge pixel. With proper thresholding of the distance map, we can get the continuous boundary as shown in Figure B.1-6. With continuous boundaries, we can label each zone as shown in Figure B.1-7. Then we can calculate the average intensity of each zone based on the original image, as shown in Figure B.1-8. For this averaged image, we

can then threshold and get the segmented Figure B.1-9. This segmented Figure B.1-9 still contains some noise from the boundary lines. With simple dilate and erode cycles, we can clean the image and get the final segmented Figure B.1-10.

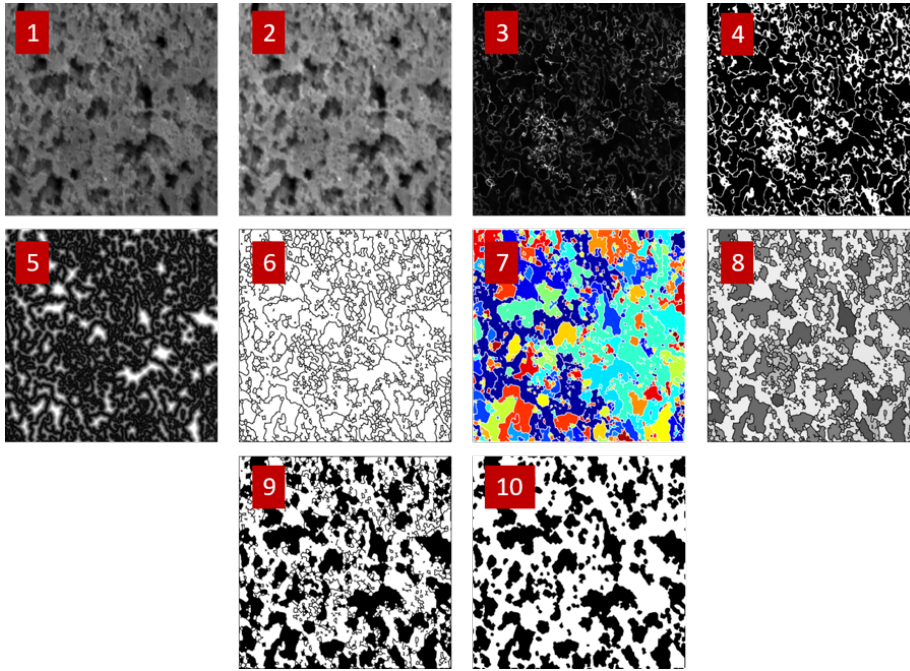


Figure B.1: SEM image segmentation based on FFT method.

It should be noted that the threshold value is important for the segmentation results. As shown in Figure B.2 are the comparison of different threshold value and their corresponding segmentation results. Figure B.2-1 is the original image. Figure B.2-3 is the histogram of the regional-averaged intensity histogram after the edge detection. As shown in Figure B.2-3 of Figure B.2, the idea threshold value should located at the valley between the lowest intensity group and the other two groups, in this case, the value is 155. Figure B.2-2 and 4 are the segmentation results with threshold value of 165 and 155. As we can see, Figure B.2-2 has some misclassification compared with Figure B.2-4.

As illustrated above, the threshold value is critical to the segmentation quality of each individual image. Through the image stack, however, histograms of different images are

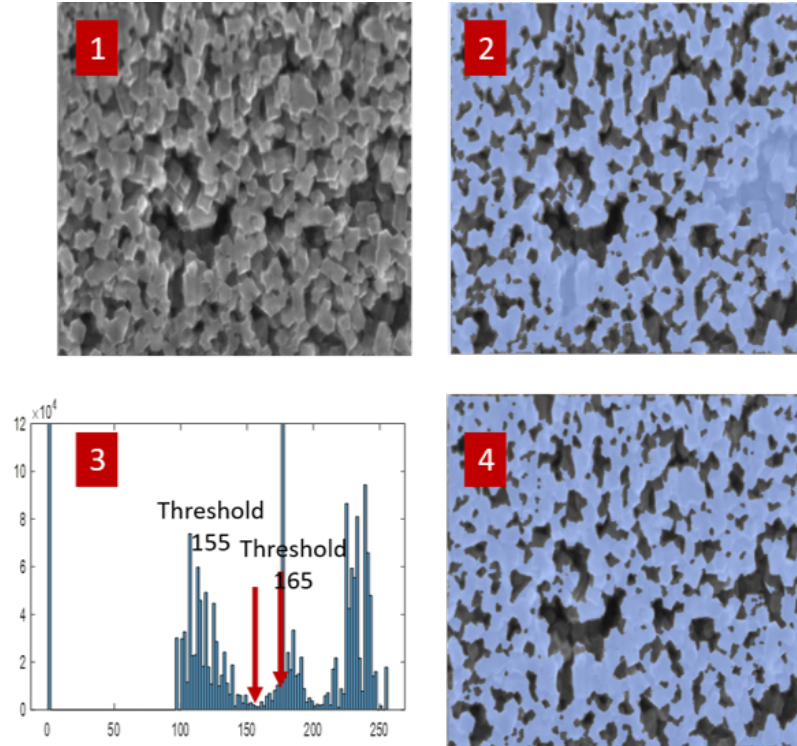


Figure B.2: Comparison of different threshold value to the segmentation results from XY plane. (1) Original image. (2) Segmentation results with threshold value of 165. (3) Histogram of the original image (4) Segmentation results with threshold value of 155.

not the same, as shown in Figure B.3-1. Using a constant threshold value may work for most of the images. But it is unavoidable to have several slides that are segmented in a wrong way, leading to discontinuous image from the YZ plane, as shown in Figure B.3-2. An updated segmentation method varies the threshold value depending on each image slide's histogram, as shown in Figure B.3-3. This adaptive thresholding method leads to improved segmentation results, as shown in Figure B.3-4.

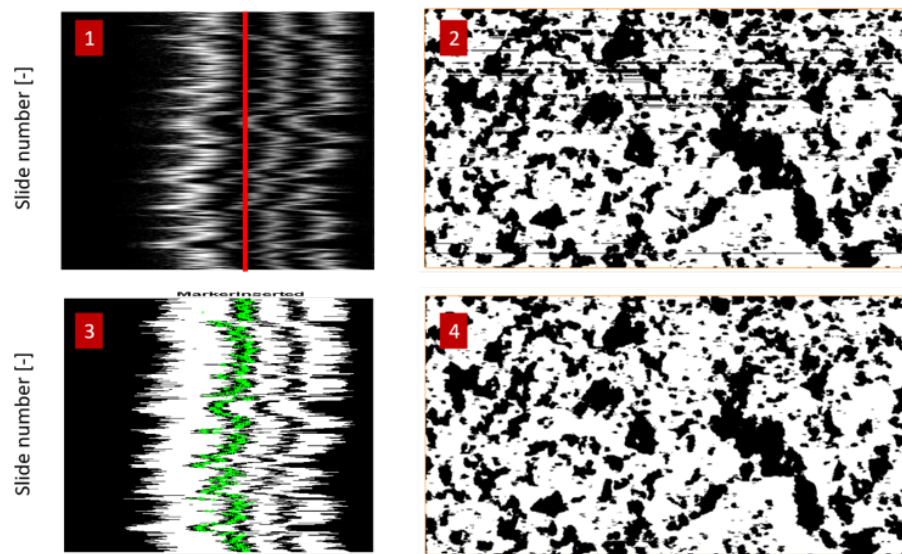


Figure B.3: Segmentation results comparison from the YZ plane (1) Histogram summary of different slides and a constant threshold value used. (2) Segmentation results with a constant threshold value used. (3) Histogram summary of different slides and threshold value was changed based on the histogram. (4) Segmentation results with varying threshold values.

Appendix C

Improving Anode Reversal Tolerance with Diode

C.1 Motivations

The advantage of diode compared with oxygen evolution reaction (OER) catalysts is that diode component are cheap and easy to integrate into the fuel cell stack. Also, it is very stable and won't degrade as fast as OER catalysts. As illustrated in Figure C.1, when there is no diode installed between the anode and the cathode, during normal operating conditions (Figure C.1a), there will be hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode. When there is hydrogen starvation at the anode (Figure C.1b), the anode reaction will be either OER or carbon corrosion reaction (COR), and the later of which can cause a lot of damage to the anode. When a diode is attached between the anode and the cathode, in normal operating conditions (Figure C.1c), the cathode has higher electrical potential compared with the anode, and the diode cannot pass electron through. When there is hydrogen starvation (Figure C.1d), the anode electrical potential starts to rise and becomes higher than the cathode electrical potential and the electrons can pass through the diode. Because of the bypassing effect of

the diode, the reaction at the anode is minimized.

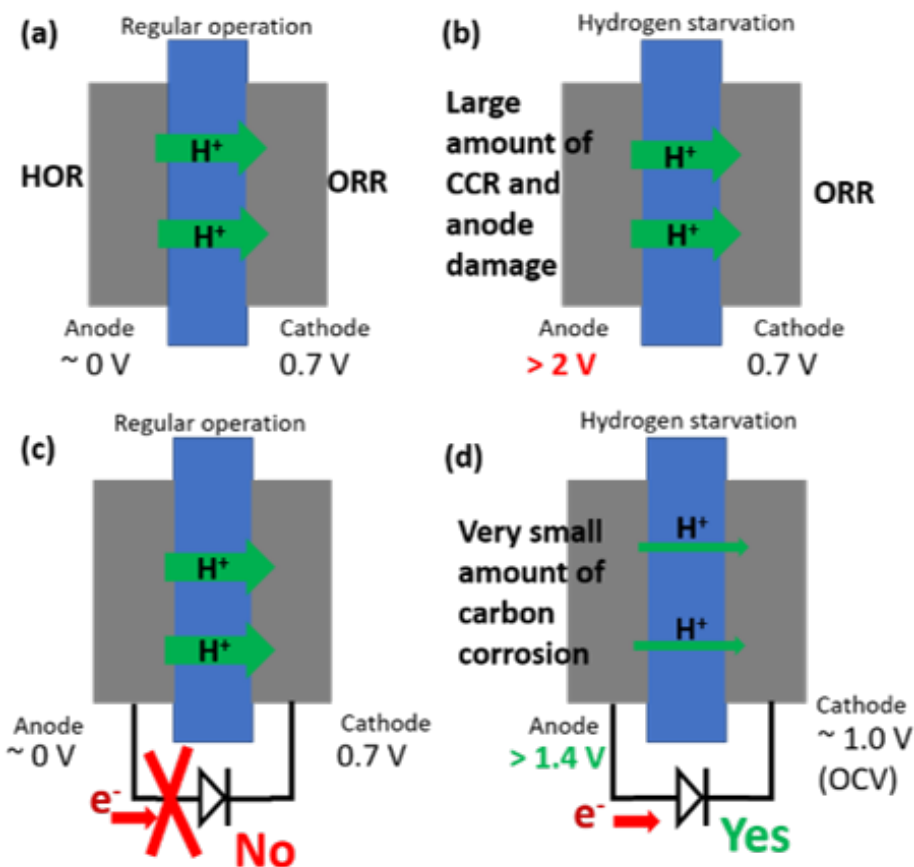


Figure C.1: Cell operating at normal conditions and under hydrogen starvation conditions with diode (c-d) and without diode (a-b).

C.2 Experiment Result and Discussion

C.2.1 Electrical Properties of Different Diodes and Configurations

Figure C.2 shows the I-V curves for different diode configurations. For a single Schottky diode, the onset potential is 0.4 V and we can see that there is exponentially increase as the cell voltage is lower than -0.4 V . For the silicon diode, the onset potential is around 0.7

V and if two silicon diodes were placed in series, the onset potential becomes 1.4 V.

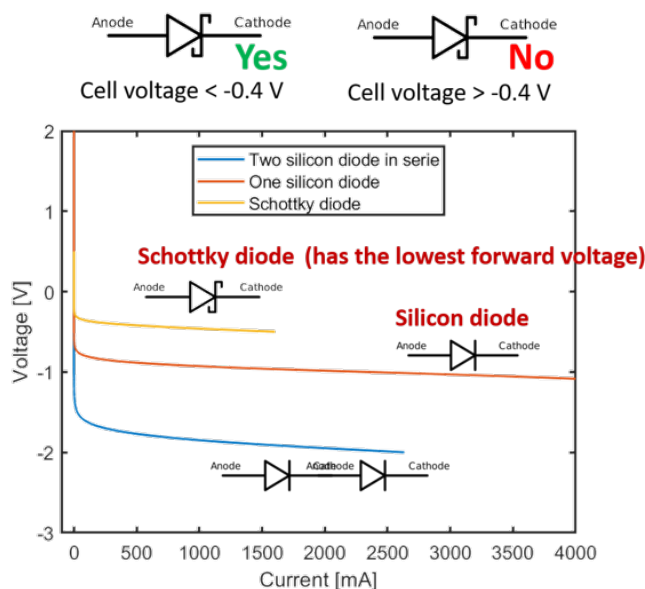


Figure C.2: The voltage vs. current plot for three different diode configurations. A single Schottky diode, a single silicon diode and two silicon diode in series.

Figure C.3 shows the zoomed-in plot of the I-V curves when cell voltage is higher than 0V, as we can see that there is a very small amount of leaking current. For Schottky diode, when the cell voltage is at 1 V, the leaking current is 0.00015 mA, which can be considered negligible and will not affect the cell performance during normal operating conditions. The polarization curve comparison with and without diode is shown in the next figure.

C.2.2 Polarization Curves Comparison With and Without Diode

Since the Schottky diode has the lowest onset potential (0.4 V), it is the most suitable diode to prevent reversal damage. Figure C.4 shows the comparison of polarization curves with a single Schottky diode (1N5822, 40V 3A DO-201AD) and without diode. The experiment was conducted with 4 cm² commercial Ion Power catalyst coated membrane (CCM) (0.3

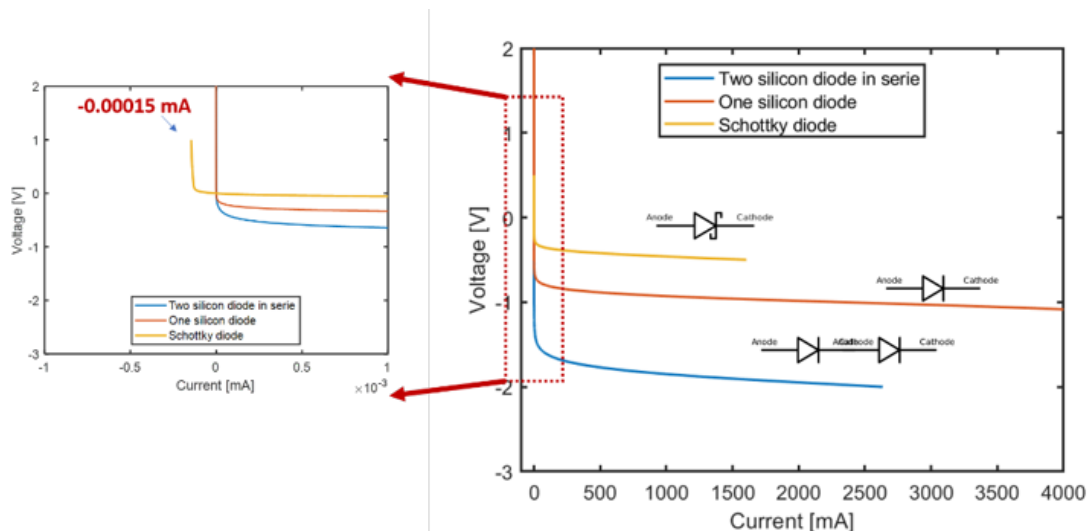


Figure C.3: The backward leaking current when cell voltage is positive.

$\text{mg}_{\text{pt}}/\text{cm}^2$). The cell temperature was 65 °C and at 100% relative humidity (RH), with a gas flow rate of 134 ml/min at that anode and 428 ml/min gas flow rate at the cathode. From the plot we can see that there is negligible difference from the polarization curves at the activation region and the Ohmic loss region. A small discrepancy comes from the high current density region, and that could be related to the instability of the cell due to flooding at high current densities. The results suggest that attaching a Schottky diode does not affect the overall performance of a single cell in normal operating conditions.

C.2.3 Cell Reversal Experiment With a Single Schottky Diode

To examine the effectiveness of the Schottky diode in preventing the reversal damage to the anode, a series of hydrogen starvation tests were conducted with a single Schottky diode (1N5822, 40V 3A DO-201AD) attached. A hydrogen reference electrode was also used to study the anode potential change during the reversal tests. The tests were conducted on a 4 cm^2 commercial Ion Power CCM ($0.3 \text{ mg}_{\text{pt}}/\text{cm}^2$) without any modification to the anode. Reversal tests were conducted at 65°C and 100% RH. The anode was supplied with

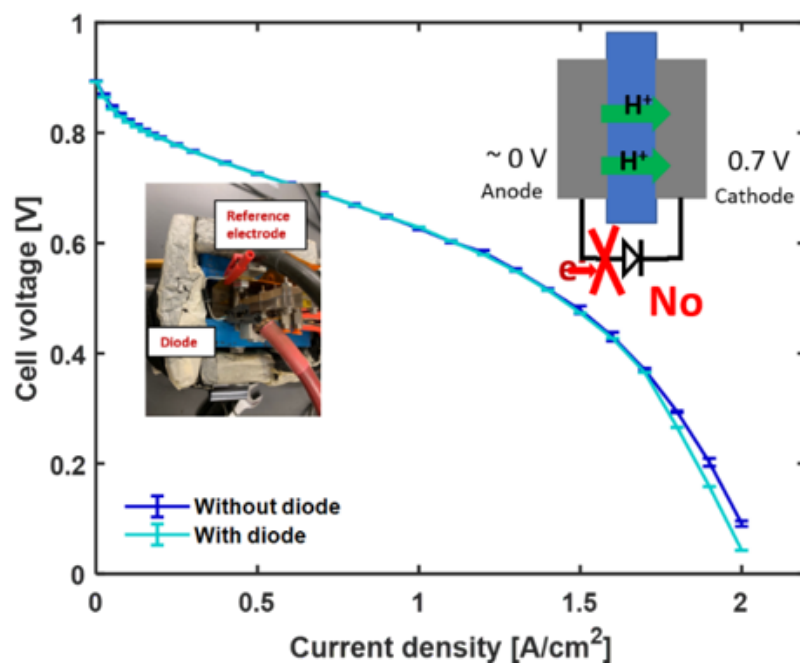


Figure C.4: The polarization curve comparison with a single Schottky diode and without diode.

hydrogen (200 ml/min) and the cathode was supplied with air (200 ml/min). Figure C.5 shows the reversal testing results. As we can see, as the hydrogen supply at the anode was cut off, the cell voltage dropped to around -0.4 V and remained stable during the entire reversal tests. Reversal tests were repeated 3 times with the same experiment parameters and no change in the cell voltage at the reversal stage. As for the anode potential, we can see that after the anode hydrogen was cut off, the anode electrode electrical potential and ionic potential difference increased from near 0.0 V to about 1.4 V in reversal state. The reason for this high anode potential is explained in the next figure.

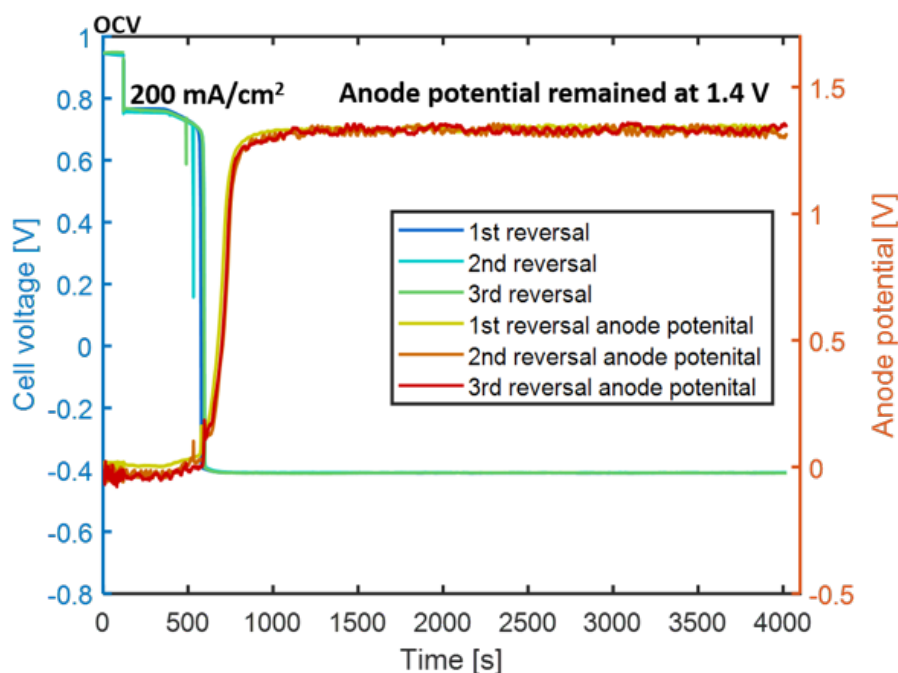


Figure C.5: Cell voltage and anode potential during hydrogen starvation tests at 65 °C and 100% RH with Schottky diode attached.

Figure C.6 shows the cell ionic potential and electrical potential distributions under normal operating conditions and under hydrogen starvation conditions with a single Schottky diode attached. As shown in Figure C.6a, under normal operating condition, when there is air supplied to the cathode, the reversible potential for ORR reaction is 1.23 V

($E_{rev} = 1.23$ V). When the cell is operated at certain current density, there is an overpotential at both the anode and the cathode based on the Tafel equation. For the anode, the HOR has very fast kinetics, thus the overpotential is very small, i.e., the difference between the anode electrical potential (E_{anode}) and the anode reversible potential (around 0 V for HOR) is small. The ORR has a slower kinetics and the difference between the cathode electrical potential ($E_{cathode}$) and the reversible potential ($E_{rev} = 1.23$ V for ORR) is relatively large. When there is hydrogen starvation, the diode bypasses most of the electrical current and there is negligible amount of Faradaic reaction at the anode and the cathode. In this case, the cathode over potential is very small and the cathode potential is very close to the value at open circuit voltage (OCV) conditions (around 1.0 V). Because the electrical current is passing through the diode, the anode electrical potential now becomes 0.4 V higher than the cathode electrical potential (around 1.4 V).

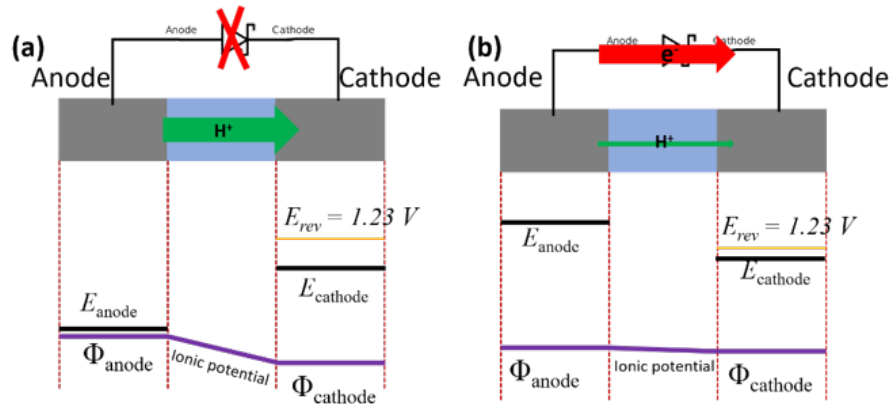


Figure C.6: Cell ionic potential and electrical potential distribution during (a) Normal operating condition (b) Hydrogen starvation condition with a single Schottky diode attached.

Figure C.7 shows characterization results of the cell after each reversal tests. Figure C.7a are polarization curves after each reversal test. As we can see, there is a noticeable amount of performance loss. The performance loss is likely to be related to the degradation of the anode at high potentials (around 1.4 V). It should be noted that this performance

loss is after hours of reversal tests. Figure C.7b are anode cyclic voltammetry (CV) curves after each reversal test. We can see a certain amount of electrochemical active surface area (ECSA) loss, but there are no significant HQ-Q peaks at 0.4 – 0.6 V potential range. From the electrochemical impedance spectroscopy (EIS) results shown in Figure C.7c, we see a slight increase of the high frequency resistance (HFR) and the charge transfer resistance. From the cathode CV curves shown in Figure C.7d, we also see a small amount of ECSA loss after each reversal test. It is possible that at anode potential of 1.4 V, there was only mild carbon corrosion, and no HQ-Q redox species were formed. The degradation of the anode could be a combination of mild carbon corrosion reaction and Pt dissolution at this anode potential.

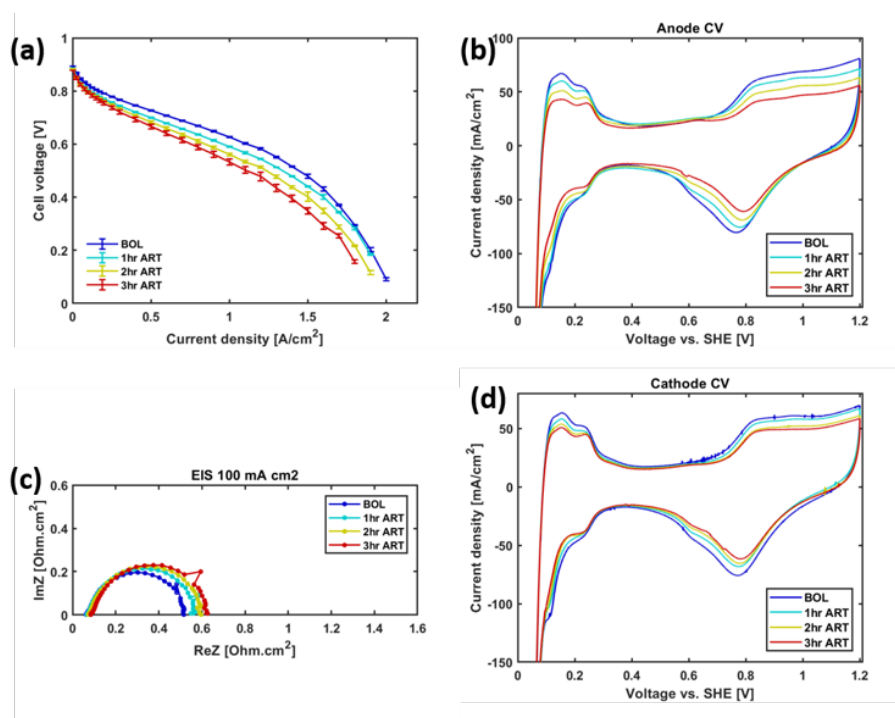


Figure C.7: Repeated hydrogen starvation tests of the Ion Power MEA with a single Schottky diode. (a) Polarization curves, (b) Anode CV curves after preconditioning and after each reversal test. (c) EIS Nyquist plots at a cell voltage of 0.5 V. (d) Cathode CV curves after preconditioning and after each reversal test.

Figure C.8 shows the comparison of the normalized cell voltage at 200 mA/cm^2 after each reversal tests. As we can see, the sample with diode attached survived three hours of hydrogen starvation and cell reversal with roughly 6% of performance loss, almost as good as the anode with Pt black + $13 \mu\text{m}$ titanium (Ti) protection layer. It should also be noted that, for the diode reversal test, the CCM used is a regular commercial Ion Power CCM with no reversal tolerant anode (RTA) catalyst added to the anode.

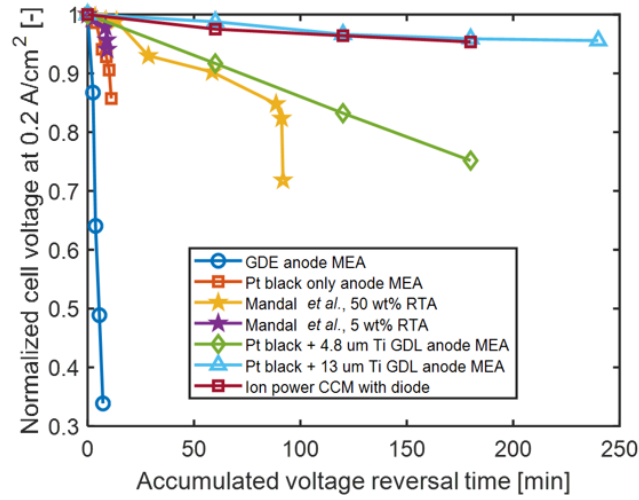


Figure C.8: Normalized cell voltage at 0.2 A/cm^2 vs. accumulated voltage reversal time. The data of the anode with an additional 5 wt% and 50 wt% IrO_2 is from work by Mandal *et al.*

C.3 Thoughts and Moving Forward

Though the Schottky diode showed promising effect in preventing reversal damage to the anode during single cell experiment, and despite the advantage of the low cost of diode and stable performance, it should be noted that the implementation might be a little bit different for a full stack contains hundreds of cells and each MEA has a much larger surface area. For the diode approach to work for a full stack, the diode must be larger to pass 200 A of

current, also. Another issue is that, when the current is bypassed by one diode attached to one cell, all the current has to go in plane through the thin bipolar plate, this might cause other problems as well.

Appendix D

Measuring Catalyst Layer Temperature During Subfreezing Hydrogen Starvation

D.1 Introduction

In Chapter 8, we studied the reversal degradation during sub-zero temperatures. From Figure 5.2 of Chapter 8, we found the intriguing result that negligible carbon corrosion would occur while the still remained at subfreezing temperatures. However, a few anecdotal results showed an eventual transition to carbon corrosion as the cell warmed due to self-heating. A better understanding of the self-heating and humidification is needed to leverage the lack of corrosion at sub-zero temperatures. Here we instrument the fuel cells with micro-thermocouples that monitor the internal cell temperature during simulated reversals. With the transient temperature change information, we can better understand the relationships between the corrosion rate and the internal heat generation and temperature within the membrane electrode assembly (MEA).

D.2 Experimental Results and Discussions

D.2.1 Temperature Sensing Experiment with a Thick Thermocouple

To monitor the anode catalyst layer temperature change, thermocouples should be placed right at the catalyst layer. However, as shown in Figure D.1, the challenge for the temperature sensing is that the thermocouple diameter is much larger than the thickness of the gasket. In order to create enough space for the thermocouple, two extra layers of Gas diffusion layer (GDL) were used, as shown in Figure D.2. The gasket's thickness is increased accordingly, with three layers of sticky polytetrafluoroethylene (PTFE) (each layer has a thickness of $170\text{ }\mu\text{m}$) layers and two layers of sticky Kapton[®] (each layer has a thickness of $60\text{ }\mu\text{m}$). Sticky Kapton[®] and PTFE are used for better gas sealing.

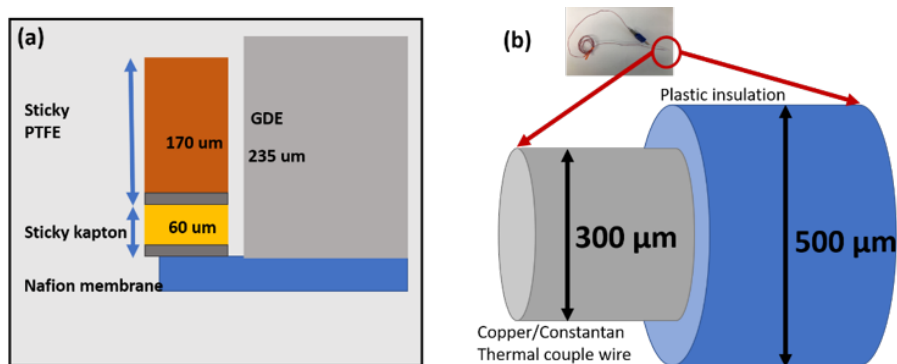


Figure D.1: (a) A GDE and gasket thickness for regular anode configuration. (b) Diameter of the thermocouple.

As shown in Figure D.3c, the inserted thermocouple has extended Kapton[®] edges at two sides of the MEA in order to provide better gas sealing. For these initial trial tests, 5 cm^2 gas diffusion electrodes (GDEs) were used as the electrode. To create good contact between the GDE and the Nafion[®] membrane, the assembled MEA was hot pressed at 130°C and 50 psi before testing. To check the performance of the MEA and the func-

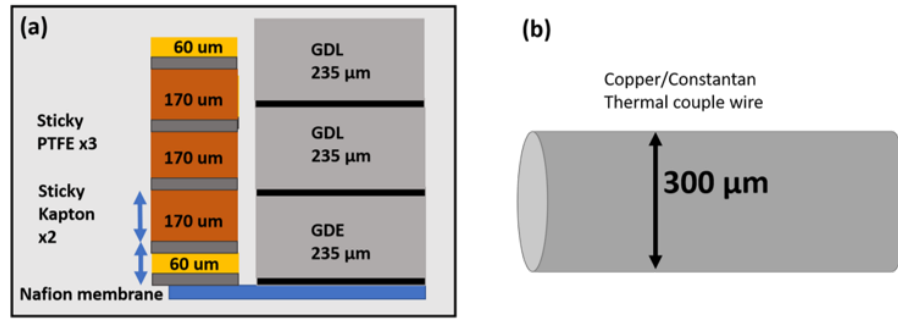


Figure D.2: (a) Increased anode thickness with two extra layers of GDLs. (b) The copper/constantan thermocouple wire diameter.

tionality of the inserted thermocouple, the cell was firstly tested at the high-temperature condition, i.e. 65°C. with a hydrogen flow rate of 200 ml/min at the anode and an air (or oxygen) gas flow rate of 550 ml/min at the cathode. Figure D.3a shows polarization curves and measured anode temperatures during air and oxygen environment measurement. We can see that the limiting current density is 1.5 A/cm² for the commercial GDE in air environment and 3.4 A/cm² in an oxygen environment, suggesting a well-functioned MEA, and that the extra thick anode configuration is not affecting too much the cell performance. Also, we can see that the thermocouple at the anode can capture the anode temperature change. As the current density increases from 0 to 1.5 A/cm², the anode temperature increased from 65°C to 67°C. While in the oxygen environment, the anode temperature increased to 72°C at the maximum current density. There is a discrepancy between the anode temperature measured by the thermocouple at hydrogen-air mode and hydrogen-oxygen mode. This could be a reason that there is more irreversible loss, and thus more heat generation at the hydrogen-air mode, as shown by the lower cell voltage at the air environment compared with the oxygen environment. But further studies will be conducted studying whether the location of the thermocouple at the cathode or at the anode will make a significant difference to the temperature measurement results. Figure

D.3b shows the cell temperature change in hydrogen pumping mode at -15°C . For the hydrogen pumping test, the anode and cathode are supplied with hydrogen gas with a flow rate of 200 ml/min. The gas passed through a humidifying bottle with room temperature (25°C) before entering the cell. During the hydrogen pumping test, the open circuit voltage (OCV) was measured for 2 min before applying current. As we can see, the cell voltage dropped very sharply after a short time of hydrogen pumping current applied. We think this might be caused by the separation of the cathode GDE with the Nafion® membrane due to the generation of hydrogen at the cathode during the hydrogen pumping process. We will use commercial catalyst coated membranes (CCMs) for the future trial test.

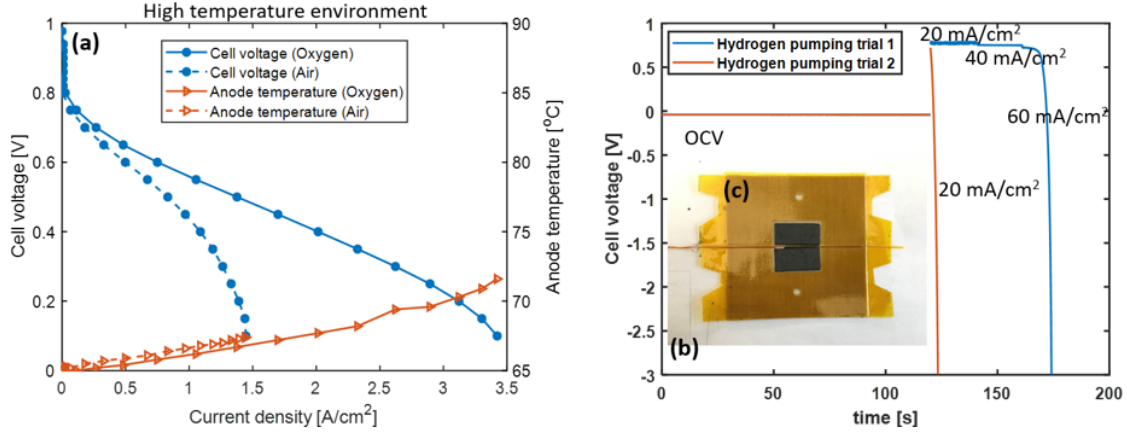


Figure D.3: (a) Polarization curves and the anode temperature change of the anode. (b) The cell voltage change at -15°C at hydrogen pumping mode. (c) Configuration of the assembled MEA, with the insertion of a thermocouple.

D.2.2 Temperature Sensing Experiment with a Thin Thermocouple

Figure D.4 shows the new anode gasket design with the thermocouple insertion. The gasket has a narrowly cut trench, and the thin thermocouple wire is planted inside the narrow trench. The thermocouple is T-type thermocouple with a wire diameter of $80\text{ }\mu\text{m}$.

To prevent the leakage of gas through the gap between the square-shaped trench and the round-shaped thermocouple wire, epoxy was filled in between the gap.

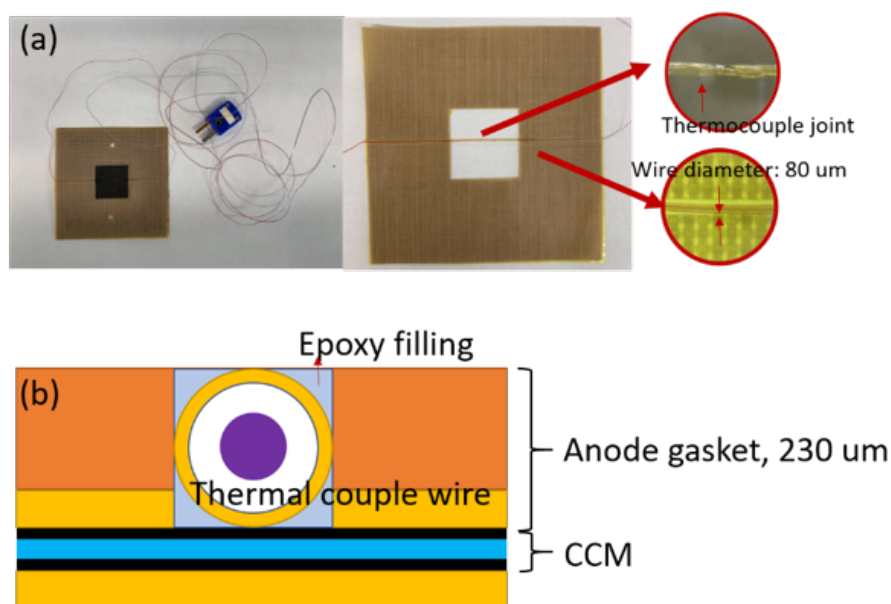


Figure D.4: The modified anode gasket with the insertion of a thermocouple. (a) Figure of the fabricated anode gasket. The thermocouple has a wire diameter of 80 μm . (b) The schematic of the cross-section of the anode gasket. The thermocouple is placed in the gasket with epoxy filling to prevent gas leaking.

Before the new thermocouple was used for subfreezing reversal experiment, it was tested for normal temperature polarization curve measurement. Figure D.5 shows the cell voltage and the anode temperature change with time. The polarization curve measurement was conducted at 65°C and 100% relative humidity (RH). The anode gas flow rate was the 134 ml/min and the cathode gas flow rate was 428 ml/min. As we can see, during the polarization curve measurement, the cell performance is normal and the temperature measurement is very stable. The measured anode temperature increased from 65°C at OCV conditions to around 67.5°C at high current density conditions. The increase in anode temperature is caused by the large amount of heat generation.

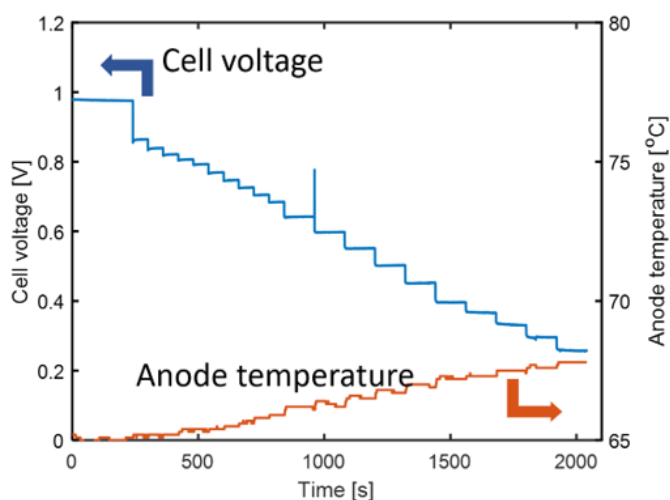


Figure D.5: Cell voltage and anode temperature change vs. time during the polarization curve measurement.

Figure D.6 shows polarization curves and the corresponding anode temperature measured in hydrogen-air and hydrogen-oxygen environment. For each case, the polarization curve was measured two times, with the reversed current flow direction and reversed gas environment, i.e. polarization curve measurement with the cathode in air/oxygen and polarization curve measurement with the anode in air/oxygen. The CCM for this measurement is commercial ion power CCM with the same platinum (Pt) loading at the anode and the cathode. The purpose of conducting these two polarization curve measurements is to study the effect of thermocouple placement to the temperature measurement. As we can see in both plots, the measured anode temperature almost overlapped with each other. Though for these two tests, the thermocouple was located at the hydrogen oxidation reaction (HOR) electrode and the oxygen reduction reaction (ORR) electrode respectively, the temperature measurement was not strongly affected.

Figure D.7 shows the cell voltage change during the subfreezing cell reversal tests and the corresponding cell temperature change. During the subfreezing reversal test, both

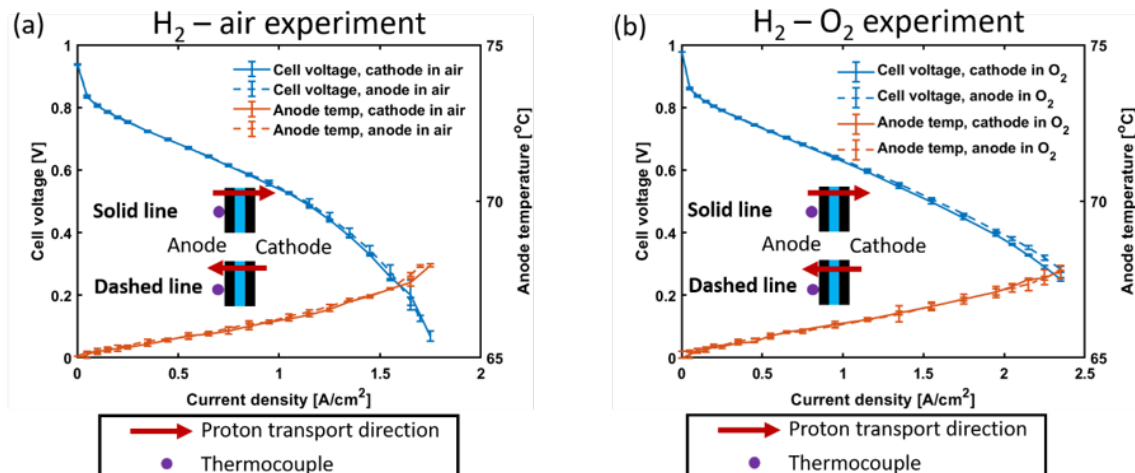


Figure D.6: The polarisation curve and the corresponding anode temperature measured in (a) Hydrogen-air environment. (b) Hydrogen-oxygen environment.

the cathode and anode are supplied with hydrogen and the cell is operated at hydrogen pumping mode. The current density used here is 200 mA/cm² and the MEA is made of commercial ion power CCM (0.3 mg_{Pt}/cm² on the anode and the cathode). As we can see here, when current is initially supplied, there is no significant change in the cell temperature. This could be attributed to the fast kinetics of HOR and the low overpotential. As we know, the speed of heat generated is related to the product of over potential and the current applied, i.e., $Q = \Delta E \times I$. After the hydrogen supply is cut off at the anode, we see a sudden drop of the cell voltage to around -1.8 to -2.0 V, corresponding to the water electrolysis reaction in this freezing condition. The water electrolysis lasted for around 30 s, and the cell voltage dropped to the cut off limit. During the reversal test. There are two sudden short increase in the cell temperature. Both these two cell temperatures increase happens when the anode reaction changes. The first temperature peak happens when the anode reaction changes from HOR to oxygen evolution reaction (OER) and the second temperature peak happens when the OER comes to an end. The sudden increase in the electrode's temperature suggests that during the reaction transition, the sudden increase

in the anode potential is a combination of electrical double layer and a overpotential increase due to the depletion of reactant, the latter of which will leads to the increase of heat generation.

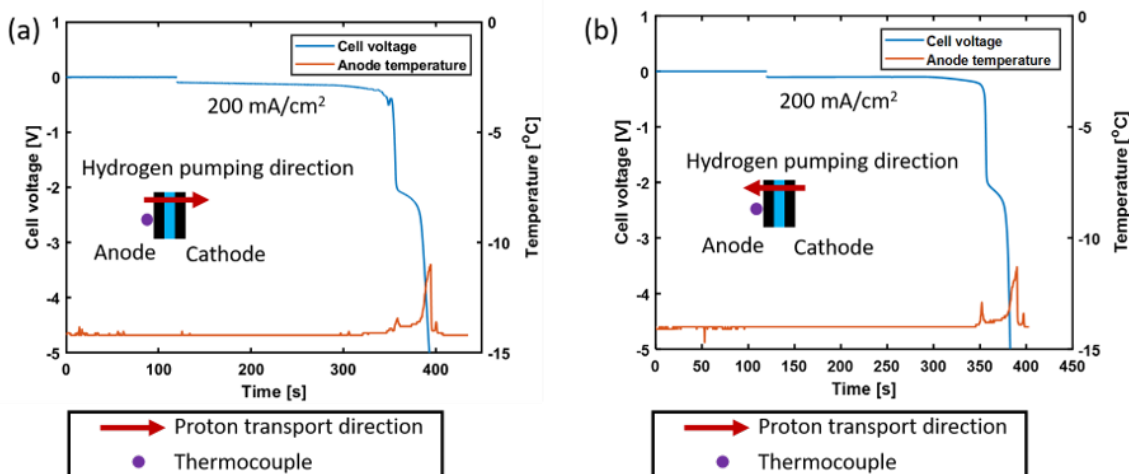


Figure D.7: Cell voltage change and the cell temperature change during subfreezing cell reversal tests at 200 mA/cm² with the thermocouple placed at (a) the anode and (b) the cathode.

Figure D.8 shows the cell voltage change during the subfreezing cell reversal tests and the corresponding cell temperature change. Compared with the cell reversal results conducted at 200 mA/cm², we can see that when current was applied to the cell before the hydrogen was cut off, the anode temperature slightly levitated and remained stable, suggesting a higher amount of heat generated compared with the 200 mA/cm² case. Similarly, as the hydrogen was cut off, we see the cell voltage dropped to the water electrolysis dominated region and then a sudden drop to the voltage cut off limit. From the anode temperature profile, we can see that there are two short temperature peaks related to the sudden change of the cell voltage, and the magnitude of the temperature increase is larger compared with 200 mA/cm² cases.

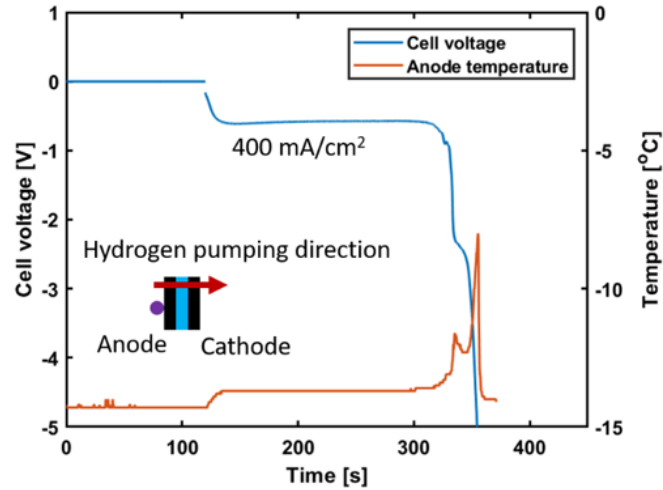


Figure D.8: Cell voltage change and the cell temperature change during subfreezing cell reversal test at 400 mA/cm² with the thermocouple placed at the anode.

D.3 Thoughts and Moving Forward

Based on these preliminary results, we think it will be helpful to conduct parameter studies on the effect of different current densities and different cell temperatures on the fuel cell hydrogen starvation damage. The understanding from these studies will help further assist the design of subfreezing start-up process.

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