An Investigation into Proton Exchange Membrane Fuel Cell Performance

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ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) has been used to diagnose fuel cells and fuel cell performances, to specifically measure changes in the electrochemical cell, as well as look at varying performance conditions. [01-05] EIS can be used to measure fuel cells performances, and to compare the theoretical electrical circuit of the cell to a Randal cell. [23]

Fuel cells are a growing choice of energy storage, because they are simple to make and easy to use. [11] A fuel cell (FC) can have many different types of exchange membranes. Here, proton exchange membrane fuel cells (PEMFC) and phosphoric acid fuel cells (PAFC) are studied due to their similarities of operation. [12] Both cells submit the catalyst to different operating conditions, which creates a different performance in a PEMFC and a PAFC. The types of catalysts can vary, but platinum catalysts and iron catalyst are particularly interesting. Platinum’s high performance comes at a high cost, [17] and iron’s ability to function as a catalyst is due to pyrolysis and chemical modification. [18-19]

To further analyze a FC, a polarization curve can be used to study the open circuit potential (OCP), the amount of potential produced for every cm² of current. Further analysis can be performed to determine the maximum power of the fuel. [09]

Fuel cells, with platinum-platinum catalyst and non-PGM iron catalyst, were constructed for a PEMFC and PAFC. The operating conditions for each type of cell were maintained through testing. Polarization data and power data revealed that a platinum-platinum cell created more power per cm² of catalyst. The iron PAFC produced no significant polarization data or EIS data. A platinum-platinum PEMFC behaved as a Randal cell, and produced more power than the non-PGM cells. All of these finding will be discussed.
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CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) has been used to study the behavior of a proton exchange membrane fuel cell [1], and EIS has been shown to be applicable in studying fuel cells. Impedance has been used to study fuel cell behavior. Multiple diagnostic tests have been performed to diagnose cells [2], and to study specific characteristics of the cell, such as temperature, gas pressure, electrode quality, and exchange membrane data. [3] Other studies have been performed to test parameters such as performance losses [4], and electrolyte loading [5], to name a few.

EIS is a measure of a system’s ability to impede the flow of electrical current. EIS applies a small voltage or current to a fuel cell. The amplitude and frequency are measured as a function of the frequency [6]. The spectra can be plotted on a Bode or Nyquist plot. When impedance is measured using a Bode plot, the resulting impedance is plotted against frequency. In a Nyquist plot, the imaginary portion of the impedance is plotted against the real impedance [7, 8]. EIS data alone cannot analyze everything about a fuel cell, so EIS is usually performed in conjunction with a polarization curve.

1.2 Polarization Curves

To further analyze a fuel cell, a polarization curve can be constructed from the polarization data obtained from the cell. A polarization curve is a plot of a cell’s performance in terms of its current density against its potential, where the current density is measured in milliamps/square centimeter and the potential is measured in volts [08].
There are three main regions to the polarization curve. The first region is considered the activation region. This region is referred to as the charge-transfer limited region. It shows the highest potential, which is also the potential with no current. This is referred to as the open circuit potential (OCP). The second region is the ohmic or kinetic region, where the curve takes on a linear slope due to ohmic losses. The equation of this region of the graph can be modeled as \( E = E^b - R_{int} \), where \( E \) is the potential, \( E^b \) is the linear extrapolation of the kinetic region, and \( I \) is the current density. The final region is the concentration potential, which is mass-transfer limited. This shows the highest current possible. In addition to this graph, the current can be graphed against the power to obtain the maximum power the cell produces [09].

Both ESI and polarization tests can be performed on any type of fuel cell, including proton exchange membrane fuel cells.

1.3 Proton Exchange Membrane Fuel Cells

The main functions of the proton exchange membrane are to conduct protons and to separate the two halves of the cell [10]. Many membrane electrode assemblies (MEA), such as an alkaline fuel cell or a molten carbonate fuel cell, push hydroxyl ions towards the anode or the carbonate anion towards the anode, respectively. The advantage that a proton exchange membrane fuel cell (PEMFC) has over another energy storage unit, such as a battery, is that it does not require recharging, and can be used over and over. [11] Most fuel cells operate by pushing an anion towards the anode, when hydrogen is flowed over the anode and oxygen is flowed over the cathode. However, PEMFC and the phosphoric acid fuel cell (PAFC) both push protons towards the cathode and create water at the cathode. [12] There are, however, subtle differences between the two.
1.4 Proton Exchange Membrane Fuel Cells vs. Phosphoric Acid Fuel Cells

PEMFCs implement an exchange membrane containing a perfluorosulfonic acid polymer electrolyte. Typically, this is a Nafion™ solution. This type of membrane has offered advantages among other types of fuel cells, such as a lighter weight, a higher catalytic activity, and no loss of electrolyte. However, this type of MEA must be constantly hydrated in order to remain conductive. Additionally, the maximum operating temperature that a PEM can exhibit is about 100°C [13]. These criteria are different from a PAFC.

PAFCs operate at temperatures between 150-190°C and pressures between atmospheric pressure to 5 atmospheres. Instead of using a perfluorosulfonic acid polymer, as in a PEMFC, a PAFC utilizes a silicon carbide matrix. To adhere the electrode to the matrix, a phosphoric acid solution is applied to each electrode [14]. Due to their high running temperature, PAFCs do not require hydration. This type of cell is already used in container packages as stationary generators [15].

Both types of cells do not emit any byproducts, excluding heat and water. Although both types of FCs use different types of polymer electrolytes, a similar, if not the same, catalyst can be used in either cell.

1.5 Catalytic Material in Fuel Cells

Many different catalysts can be used in fuel cell development. Out of all the possible catalysts, the most effective catalyst is a platinum catalyst, with a current density of 500 mA/cm² at a loading of 4 mg Pt/cm². This is a great deal of current for such a low area, but the cost for such efficiency is about $400/kW of power [16]. Additionally, the cost of platinum, as of 2006, was $45/gram [17]. In order to minimize this cost, non-platinum catalysts can be substituted for platinum, which typically are palladium or ruthenium, but are both expensive. Alternatively,
platinum can be replaced by a non-precious or non-platinum group metal (non-PGM) that is relatively inexpensive. Cobalt and iron are the two most commonly used non-PGM.

To improve upon the activity of such catalysts, cobalt and iron can undergo pyrolysis, or heating without oxygen, to form metallic iron and cobalt cores surrounded by a tetrad of nitrogen atoms. Often, these pyrolyzed groups are on a carbon support or carbon backing [18]. Iron seems to have a larger potential. Jaouen et al. have reported that the four requirements for an active iron catalyst are iron, nitrogen, disordered carbon, and a microporous catalytic layer [19].

To use this type of iron catalyst, gases are flowed over the cathode and anode. There are different types of medium or backings that can be used to contain the catalysts and form the electrode assembly.

1.6 Electrode Materials

Many materials which support catalysts in fuel cell electrodes are made of some form of carbon. Carbon nanotubes (CNT), specifically carbon black nanotubes, are a favorable material in electrodes, due to their nanosized pores, which allow for a maximum surface area of the chosen catalysts and a maximum electrochemical reactivity [19]. This backing is referred to as the gas diffusion layer (GDL). Once this is loaded with a catalyst, the GDL becomes a gas diffusion electrode (GDE). GDL material can be made from carbon paper or carbon cloth [20]. However, given that carbon cloth is woven, it is more porous and able to accept more catalyst per CNT and a better dispersion of Nafion™ binder.

Once the GDL is loaded with a catalyst to become a GDL and attached to an exchange membrane, gases need to be flowed over the assembly to fuel the cell and produce power.
1.7 Fuel Cell Fuel Choices

In order to operate and test a fuel cell, specific gases need to be flowed over the electrode. Those gases flowed over the cathode are reduced, and those flowed over the anode are oxidized. The typical gases used for performance analysis are hydrogen and oxygen, which act as the fuel and the oxidant, respectively [21]. Hydrogen and oxygen both provide amazing electrode kinetics. However, in order to lower the costs of fuel, other gases have been used, namely hydrocarbons and alcohols, in place of hydrogen [22]. However, hydrogen and oxygen fully oxidize and reduce each other into water, which is why they are the fuel of choice. The fuel of choice must be matched with a catalyst of choice.

1.8 Chosen Catalysts

As stated earlier, platinum is the most efficient catalyst for FCs. But how do non-PGM catalysts compare to platinum? Testing a non-PGM catalyst alongside testing platinum would produce comparable data for the two, and a decision of the efficiency of the catalysts could be made. One such iron catalyst from Pajarito Powder is of interest. It has been tested as a PEMFC in the past, but not as a PAFC. Creating a PEMFC and a PAFC, and testing them alongside of a Pt-Pt PEMFC and a Pt-PT PAFC should yield interesting results, and is the purpose of this research.

1.9 Research Aims

With two types of MEAs of interest, and variable characteristics of performance, FCs can be optimized by varying these conditions. The type of catalyst, operating conditions, and fuel choice are just a few variable characteristics that can enhance or inhibit the performance of a FC.
The overall objective was to perform a polarization test and EIS on four cells in total: a Pt-Pt PEMFC, Pt-Pt PAFC, a non-PGM PEMFC and a non-PGM PAFC. The first objective was to successfully create a platinum-platinum PAFC, a platinum-platinum PEMFC, an iron-platinum PAFC, and an iron-platinum PEMFC. The second objective was to obtain polarization data from both FCs to gather performance data on the MEA, using hydrogen and oxygen as fuel. The third objective was to obtain ESI data on all four cells. And finally, the last objective was to analyze and compare the data of the MEAs to show how a non-pgm PGM and PAFC compares to a platinum PEM and PAFC.
CHAPTER 2: MATERIALS AND METHODS

2.1 Phosphoric Acid Platinum Fuel Cell Testing

2.1.1 Exchange Membrane Preparation

An AP-205 membrane, from Advent Technologies was cut down to 7.5x7.5cm and the mass of the membrane was obtained using an Ohas Explorer mass balance. The membrane was transferred to a crystalizing dish. An excess amount of 85% orthophosphoric acid, from Alfa Aesar, was poured over the membrane. A petri dish was used to flatten the membrane and hold it stationary at the bottom of the large glass container. The assembly was transferred into a larger crystalizing dish containing organic mineral oil from Alfa Aesar. This was then placed on a heating plate from IKA and heated to 120°C, with the emergency cutoff temperature set to 145°C. The membrane soaked in phosphoric acid overnight. The membrane was then removed from the phosphoric acid, dried, and a mass was taken. The phosphoric acid loading was calculated by taking the differences of the masses and dividing by the area of the membrane.

2.1.2 Electrode Preparation

An E-TEK LT140W-W.020904 gas diffusion electrode (GDE), with a loading of 0.35 mg/cm² of platinum, was cut down into 2-2.5x2.5 cm square anodes. The mass of the dry anodes was taken and was adhered to a heating plate at a temperature of 150°C.

2.1.3 Electrode Spraying

Using a spray-gun, which was cleaned using 2-propanol, a solution of phosphoric acid in 2-propanol was sprayed onto the anodes, powered by compressed nitrogen from Middlesex Gases and Technologies Inc. Spraying was regulated to allow for an even distribution of solution and
drying in between sprays. Once the loading of phosphoric acid was at 0.35 mg/cm², each anode was allowed to dry for ten minutes.

2.1.4 Electrode Assembly

Upon complete drying of both anodes, the two were prepared for electrode pressing. The phosphoric acid soaked membrane was placed between two FEP sub-gaskets from Advent Technologies. A 2.1x2.2 cm hole was cut out of the sub-gaskets. The anodes were placed on either side, allowing for direct contact between the electrode and the phosphoric acid membrane. Then, two thicker Teflon gaskets, precut to expose the electrode, were used to contain the rest of the assembly. Once all of the gaskets were applied, the assembly was placed in the middle of two metal press plates. A Carver Hydraulic Unit (Model # 3912) was used to press the electrode, using a pressing procedure.

2.1.5 Pressing Procedure

The heat to both plates of the hydraulic unit was turned on and allowed to come to 60°C. At this temperature, the pressing assembly was placed in between the heated press plates. About 5086 pounds of force was applied to the plates at 60°C for 10 minutes. The temperature was raised to 75°C and held constant for another 10 minutes. Next, the temperature was set to 90°C for 20 minutes. The next temperature and time settings were 110°C for 15 minutes and 150°C for 10 minutes respectively. After the 10 minutes at 150°C, the pressure was increased to 11,444 pound force at 150°C and held for 15 minutes. The heat was powered off, and the temperature of the press was cooled to 60°C, as the pressure remained a constant 11,444 pound force. Table 1 shows a detailed list of the necessary temperatures, pressures, and times used to assemble the
electrode. The electrode pressing plates were removed from the hydraulic press and allowed to cool to 25\(^{\circ}\)C.

<table>
<thead>
<tr>
<th>Temperature ((^{\circ})C)</th>
<th>60</th>
<th>75</th>
<th>90</th>
<th>110</th>
<th>150</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (lbf)</td>
<td>5086</td>
<td>5086</td>
<td>5086</td>
<td>5086</td>
<td>5086</td>
<td>11444</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

Temperatures were held as constant as possible. The pressure was adjusted occasionally to maintain the given values.

2.1.6 Fuel Cell Assembly

The assembled PAFC electrode was removed from the large press plates. Using a cutting template created by previous graduate students the electrode was cut down to fit inside a FC-05-02 cell housing with a serpentine flow field pattern. The electrode was placed directly over the flow fields.

The main body of the housing was then closed around the flow blocks. The bolts were first manually tightened, and then were tightened using a CDI torque wrench, set to 20 pounds of force. The tightening procedure was performed using a star-pattern, to allow for even distribution of the tightening.

2.1.7 Test Station

The cell housing was hooked up to a test station, built and maintained by graduate students. The station was turned on, and the temperature was set to 100\(^{\circ}\)C. Once at the desired temperature, hydrogen gas was flowed over the cathode and oxygen gas was flowed over the anode. The temperature of the cell was raised to 180\(^{\circ}\)C. The back pressure was set to 0 PSI.
2.1.8 Testing Hardware and Software

Alligator clips were attached to the top of the cell, connected to a Hewlett Packard 6050A1800 Watt dc Electronic Load Mainframe. Once the cell was at temperature, an open current potential (OCP) test was performed to measure the amount of voltage, without applying a current. After 5 minutes, the Labview OCP was recorded, and the program was terminated. A Labview Potentiostatic control graph was then run. The potential was set to 0.7 volts and held constant for 1 hour. The potential was stepped down to 0.6, 0.5, and 0.4 volts, and held at these potentials for 10 minutes each. The current was recorded after each 10 minute interval. Next, the potential was stepped down to 0.3, 0.2, and 0.1 volts, and held at these potentials for 1 minute, each. The current was recorded after each 1 minute interval. The potential was then increased by 0.1 volts every 45 seconds, up to 0.7 volts, where the program was terminated.

A Galvanostatic polarization curve on Labview was then performed. The current from the 0.2 step in the Potentiostatic control was set as the region II upper limit, and a third of that value was set to the region I upper limit. The values of the differential current I and II were set to 0.01 amps and 0.05 amps respectively. Wait time I and II were both set to 10 seconds. The program was run to completion. The program was terminated, and the alligator clips were disconnected from the cell housing.

An EZStat Pro was then hooked up to the cell housing. The EZStat Pro application was used to first measure the OCP for 10 seconds. Then, 50 current data points were measured every 30 seconds. Once completed, the program was terminated, and the EZ Stat was disconnected from the cell housing.
A Labview Potentiostat/Galvanostat, hooked up to a Labview 20A current booster, was attached to the cell housing. NOVA 1.10.1.9 was launched, and Galvanostatic impedance was run, gathering 25 data points at 10, 40, 100, 200, 300, 600, 800, and 1000 mAmps respectively. Once this data was collected, Nova was terminated and the hardware was disconnected from the cell housing.

2.2 Proton Exchange Membrane Platinum Fuel Cell Testing

2.2.1 Electrode Preparation

An E-TEK LT140W-W.020904 gas diffusion electrode (GDE), with a loading of 0.35 mg/cm² of platinum, was cut down into 2-2.5x2.5 cm square anodes. The mass of the dry anodes was recorded and was adhered to a heating plate at a temperature of 150°C.

2.2.2 Contact Solution Preparation

A sample of 2 mL of 2-propanol was added to each vial, along with 280uL of Nafion D-521. Both of these vials were sonicated for 10 minutes.

2.2.3 Electrode Spraying

Using a spray-gun, which was cleaned using 2-propanol, the binding solution was sprayed onto the electrodes. Spraying was regulated to allow for an even distribution of contact solution and drying in between sprays. Once all of the ink as transferred onto the cathode, it was allowed to dry for ten minutes.

The anodes were removed from the heating plate and the mass of the sprayed cathode was taken. The cathode and anode were then adhered back to the heat plate. A vial of contact solution was sprayed onto each square, allowing for adequate drying.
2.2.4 Electrode Assembly

Once the entire contact layer was dried, the cathode and anode were both cut down to 2.2x2.1 cm. A Nafion-211 membrane from Ion Power, with a thickness of 0.001 inches, was cut down to a 3.0x3.0 cm square. The protective film was removed from each side, and the exposed exchange membrane was placed in between the cathode and anode, with the sprayed portions facing the membrane. This was then placed in a small press plate and padded with weigh paper from Whatman. A Carver Hydraulic Unit (Model # 3912) was used to press the electrode.

2.2.5 Pressing Procedure

The heat to both plates of the hydraulic unit was turned on and allowed to come to 135°C. At this temperature, the pressing assembly was placed in between the heated press plates. About 1000 pounds of force was applied to the plates at 135°C for 5 minutes. Table 2 gives a detailed display of pressure, temperature, and time necessary to press the PEM membrane. The pressure was released and the electrode pressing plates were removed from the hydraulic press and allowed to cool at 25°C. The electrode was carefully removed from the press plates.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (lbf)</td>
<td>5086</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2: Temperature and Pressure Procedure for PEM Electrodes

Temperature was held as constant as possible. The pressure was adjusted occasionally to maintain the given value.
2.2.6 Gasket Cutting

Two 6”x6” squares of fiberglass gaskets, from Saint Gobian Performance Plastics, were individually placed on to a cutting plate. A cutting template, build by graduate students, was placed on top of the fiberglass material. This was placed onto the hydraulic press and compressed to 1000 pounds for 10 seconds. The pressure was released. This process was repeated for the second gasket. The newly cut gaskets were removed from the template and cleaned of any debris.

2.2.7 Fuel Cell Assembly

The assembled PEM electrode was placed inside a FC-05-02 cell housing with a serpentine flow field pattern. A fiberglass gasket was placed on either side of the flow block to allow adequate sealing of the cell housing. The electrode was placed directly over the flow fields on the fiberglass gaskets. The main body of the housing was then closed around the flow blocks. The bolts were first manually tightened, and then were tightened using a CDI torque wrench, set to 20 pounds of force. The tightening procedure was performed using a star-pattern, to allow for even distribution of the tightening.

2.2.8 Test Station

The cell housing was hooked up to a test station, built and maintained by graduate students. The station was turned on, and the heat rate was set to 15%. The temperature of the cell housing was set to 85°C. Nitrogen was flowed into the cell station, on both the cathode and anode, for 45 minutes. Nitrogen was then turned off. Hydrogen gas was flowed over the cathode and oxygen gas was flowed over the anode. The temperature of the cell maintained at 85°C. The back pressure was set to 0 PSI.
2.2.9. Testing Hardware and Software

Alligator clips were attached to the top of the cell, connected to a Hewlett Packard 6050A1800 Watt dc Electronic Load Mainframe. Once the cell was at temperature, an open current potential (OCP) test was performed to measure the amount of voltage, without applying a current. After 5 minutes, the Labview OCP was recorded, and the program was terminated. A Labview Potentiostatic control, with a graph, was then run. The potential was set to 0.7 volts and held constant for 1 hour. Then, the potential was stepped down to 0.6, 0.5, and 0.4 volts, and held at these potentials for 10 minutes, each. The current was recorded after each 10 minute interval. The potential was stepped down to 0.3, 0.2, and 0.1 volts, and held at these potentials for 1 minute, each. The current was recorded after each 1 minute interval. The potential was then increased by 0.1 volts every 45 seconds, up to 0.7 volts, where the program was terminated.

A Galvanostatic polarization curve on Labview was then performed. The current from the 0.2 ampere step in the Potentiostatic control was set as the region II upper limit, and a third of that value was set to the region I upper limit. The values of the differential current I and II were set to 0.01 amps and 0.05 amps, respectfully. Wait time I and II were both set to 10 seconds. The program was run to completion. The program was terminated, and the alligator clips were disconnected from the cell housing.

An EZStat Pro was then hooked up to the cell housing. The EZStat Pro application was used to first measure the OCP for 10 seconds. Then, 50 current data points were measured every 30 seconds. Once completed, the program was terminated, and the EZ Stat was disconnected from the cell housing.
A Labview Potentiostat/Galvanostat, hooked up to a Labview 20A current booster, was attached to the cell housing. NOVA 1.10.1.9 was launched, and Galvanostatic impedance was run, gathering 25 data points at 10, 40, 100, 200, 300, 600, 800, and 1000 mAmps, respectively. Once this data was collected, Nova was terminated and the hardware was disconnected from the cell housing.

The back pressure was then turned up to 28 psi and the data was collected the same way. This was then repeated at 40 psi.

2.3 Phosphoric Acid Non-PGM Fuel Cell Testing

2.3.1 Exchange Membrane Preparation

An AP-205 membrane, from Advent Technologies, cut down to a 7.5x7.5cm and the mass of the membrane was obtained using an Ohas Explorer mass balance. The membrane was transferred to a crystalizing dish. An excess amount of 85% orthophosphoric acid, from Alter Aesar, was poured over the membrane. A petri dish was used to flatten the membrane and hold it stationary at the bottom of the large glass container. The assembly was transferred into a larger crystalizing dish containing organic mineral oil from Alfa Aesar. This was then placed on a heating plate from IKA and heated to 120°C, with the emergency cutoff temperature set to 145°C. The membrane soaked in phosphoric acid overnight. The membrane was then removed from the phosphoric acid, dried, and a mass was taken. The phosphoric acid loading was calculated by taking the differences of the masses and dividing by the area of the membrane.

2.3.2 Electrode Preparation
An E-TEK LT140W-W.020904 gas diffusion electrode (GDE), with a loading of 0.35 mg/cm$^2$ of platinum, was cut down into a 2-2.5x2.5 cm square anode. An E-TEK LT1400-W.030906 GDL was cut down into a 2.5x2.5 cm square cathode. The mass of the dry cathode and anode was taken and the cathode was adhered to a heating plate at a temperature of 150°C.

2.3.3. Ink Preparation

A 50.0 mg sample of Pajarito Powder catalyst was obtained. This sample was to a mixture of 8.5 ml of isopropanol from Alta Aesar and 1.5 mL of deionized water. This ink solution was sonicated for one hour.

2.3.4 Spray Procedure

Using a spray-gun, which was cleaned using 2-propanol, the ink solution was sprayed onto the cathode, powered by compressed nitrogen from Middlesex Gases and Technologies Inc. Spraying was regulated to allow for an even distribution of ink and drying in between sprays. Once all the ink was sprayed, the cathode was allowed to dry for ten minutes. The cathode was then weighted and the ink solution loading was calculated.

Once the loading of ink was known, the cathode was adhered back to the heating plate. A solution of phosphoric acid in isopropanol was sprayed onto the cathode, so that the phosphoric acid loading was the same as the catalyst loading. Once the desired loading was obtained, the cathode was removed and the anode was adhered to the plate. The anode was sprayed with phosphoric acid solution, such that the loading of phosphoric acid was equal to the loading of platinum on the anode, 0.35 mg/cm$^2$. The anode was allowed to dry.
2.3.5 Electrode Assembly

Upon complete drying of both cathode and anode, the two were prepared for electrode pressing. The phosphoric acid soaked membrane was placed between two FEP sub-gaskets from Advent Technologies. A 2.1x2.2 cm hole was cut out of the sub-gaskets. The cathode and anode were placed on either side, allowing for direct contact between the electrode and the phosphoric acid membrane. Two thicker Teflon gaskets, precut to expose the electrode, were used to contain the rest of the assembly. Once all of the gaskets were applied, the assembly was placed in the middle of two metal press plates. A Carver Hydraulic Unit (Model # 3912) was used to press the electrode, using a pressing procedure.

2.3.6 Pressing Procedure

The heat to both plates of the hydraulic unit was turned on and allowed to come to 60°C. At this temperature, the pressing assembly was placed in between the heated press plates. About 5086 pounds of force was applied to the plates at 60°C for 10 minutes. The temperature was raised to 75°C and held constant for another 10 minutes. Next, the temperature was set to 90°C for 20 minutes. The next temperature and time settings were 110°C for 15 minutes and 150°C for 10 minutes respectfully. After the 10 minutes at 150°C, the pressure was increased to 11,444 pound force at 150°C and held for 15 minutes. The heat was powered off, and the temperature of the press was cooled to 60°C, as the pressure remained a constant 11,444 pound force. Table 1 shows a detailed list of the necessary temperatures, pressures, and times used to assemble the electrode. The electrode pressing plates were removed from the hydraulic press and allowed to cool to 25°C.
2.3.7 Fuel Cell Assembly

The assembled PAFC electrode was removed from the large press plates. Using a cutting template, created by previous graduate students, the electrode was cut down to fit inside a FC-05-02 cell housing with a serpentine flow field pattern. The electrode was placed directly over the flow fields.

The main body of the housing was then closed around the flow blocks. The bolts were first manually tightened, and then were tightened using a CDI torque wrench, set to 20 pounds of force. The tightening procedure was performed using a star-pattern, to allow for even distribution of the tightening.

2.3.8 Test Station

The cell housing was hooked up to a test station, built and maintained by graduate students. The station was turned on, and the heat was to 100°C. Once at the desired temperature, hydrogen gas was flowed over the cathode at and oxygen gas was flowed over the anode. The heat of the cell was raised to 180°C. The back pressure was set to 0 PSI.

2.3.9 Testing Hardware and Software

Alligator clips were attached to the top of the cell, connected to a Hewlett Packard 6050A 1800 Watt dc Electronic Load Mainframe. Once the cell was at temperature, an open current potential (OCP) test was performed to measure the amount of voltage, without applying a current. After 5 minutes, the Labview OCP was recorded, and the program was terminated. A Labview Potentiostatic control graph was then run. The potential was set to 0.7 volts and held constant for 1 hour. The potential was stepped down to 0.6, 0.5, and 0.4 volts, and held at these potentials for
10 minutes, each. The current was recorded after each 10 minute interval. Next, the potential was stepped down to 0.3, 0.2, and 0.1 volts, and held at these potentials for 1 minute, each. The current was recorded after each 1 minute interval. The potential was then increased by 0.1 volts every 45 seconds, up to 0.7 volts, where the program was terminated.

A Galvanostatic polarization curve on Labview was then performed. The current from the 0.2 step in the Potentiostatic control was set as the region II upper limit, and a third of that value was set to the region I upper limit. The values of the differential current I and II were set to 0.01 amps and 0.05 amps, respectfully. Wait time I and II were both set to 10 seconds. The program was run to completion. The program was terminated, and the alligator clips were disconnected from the cell housing.

An EZStat Pro was then hooked up to the cell housing. The EZStat Pro application was used to first measure the OCP for 10 seconds. Then, 50 current data points were measured every 30 seconds. Once completed, the program was terminated, and the EZ Stat was disconnected from the cell housing.

A Labview Potentiostat/Galvanostat, hooked up to a Labview 20A current booster, was attached to the cell housing. NOVA 1.10.1.9 was launched, and Galvanostatic impedance was run, gathering 25 data points at 10, 40, 100, 200, 300, 600, 800, and 1000mAmmps respectfully. Once this data was collected, Nova was terminated and the hardware was disconnected from the cell housing.

2.4 Proton Exchange Membrane Non-PGM Fuel Cell Testing

2.4.1 Electrode Preparation
An E-TEK LT140W-W.020904 gas diffusion electrode (GDE), with a loading of 0.35 mg/cm$^2$ of platinum, was cut down into 2-2.5x2.5 cm square anodes. The mass of the dry anodes was recorded and was adhered to a heating plate at a temperature of 150$^\circ$C.

2.4.2 Contact Solution Preparation

A sample of 2 mL of 2-propanol was added to each vial, along with 280uL of Nafion D-521. Both of these vials were sonicated for 10 minutes.

2.4.3 Ink Preparation

A 50.0 mg sample of Pajarito Powder catalyst was obtained. This sample was to a mixture of 8.5 ml of isopropanol from Alta Aesar and 1.5 mL of deionized water. This ink solution was sonicated for one hour.

2.4.4 Electrode Spraying

Using a spray-gun, which was cleaned using 2-propanol, the ink solution was sprayed onto the cathode, powered by compressed nitrogen from Middlesex Gases and Technologies Inc. Spraying was regulated to allow for an even distribution of ink and drying in between sprays. Once all the ink was sprayed, the cathode was allowed to dry for ten minutes. The cathode was then weighted and the ink solution loading was calculated.

The cathode and anode were removed from the heating plate and the mass of the sprayed cathode was taken. The cathode and anode were then adhered back to the heat plate. A vial of contact solution was sprayed onto each square, allowing for adequate drying.

2.4.5 Electrode Assembly
Once the entire contact layer was dried, the cathode and anode were both cut down to 2.2x2.1 cm. A Nafion-211 membrane, with a thickness of 0.001 inches, was cut down to a 3.0x3.0 cm square. The protective film was removed from each side, and the exposed exchange membrane was placed in between the cathode and anode, with the sprayed portions facing the membrane. This was then placed in a small press plate and padded with weigh paper from Wattman. A Carver Hydraulic Unit (Model # 3912) was used to press the electrode.

2.4.6 Pressing Procedure

The heat to both plates of the hydraulic unit was turned on and allowed to come to 135°C. At this temperature, the pressing assembly was placed in between the heated press plates. About 1000 pounds of force was applied to the plates at 135°C for 5 minutes. Table 2 gives a detailed display of pressure, temperature, and time necessary to press the PEM membrane. The pressure was released and the electrode pressing plates were removed from the hydraulic press and allowed to cool at 25°C. The electrode was carefully removed from the press plates.

2.4.7 Gasket Cutting

Two 6”x6” squares of fiberglass gaskets, from Saint Gobian Performance Plastics, were individually placed on to a cutting plate. A cutting template, build by graduate students, was placed on top of the fiberglass material. This was placed onto the hydraulic press and compressed to 1000 pounds for 10 seconds. The pressure was released. This process was repeated for the second gasket. The newly cut gaskets were removed from the template and cleaned of any debris.
2.4.8 Fuel Cell Assembly

The assembled PEM electrode was placed inside a FC-05-02 cell housing with a serpentine flow field pattern. A fiberglass gasket was placed on either side of the flow blow, to allow adequate sealing of the cell housing. The electrode was placed directly over the flow fields on the fiberglass gaskets. The main body of the housing was then closed around the flow blocks. The bolts were first manually tightened, and then were tightened using a CDI torque wrench, set to 20 pounds of force. The tightening procedure was performed using a star-pattern, to allow for even distribution of the tightening.

2.4.9 Test Station

The cell housing was hooked up to a test station, built and maintained by graduate students. The station was turned on, and the heat rate was set to 15%. The temperature of the cell housing was set to 85°C. Nitrogen was flowed into the cell station, on both the cathode and anode, for 45 minutes. Nitrogen was then turned off. Hydrogen gas was flowed over the cathode and oxygen gas was flowed over the anode. The heat of the cell maintained at 85°C. The back pressure was set to 0 PSI.

2.4.10 Testing Hardware and Software

Alligator clips were attached to the top of the cell, connected to a Hewlett Packard 6050A1800 Watt dc Electronic Load Mainframe. Once the cell was at temperature, an open current potential (OCP) test was performed to measure the amount of voltage, without applying a current. After 5 minutes, the Labview OCP was recorded, and the program was terminated. A Labview Potentiostatic control, with a graph, was then run. The potential was set to 0.7 volts and held constant for 1 hour. Then, the potential was stepped down to 0.6, 0.5, and 0.4 volts, and held at
these potentials for 10 minutes, each. The current was recorded after each 10 minute interval. The potential was stepped down to 0.3, 0.2, and 0.1 volts, and held at these potentials for 1 minute, each. The current was recorded after each 1 minute interval. The potential was then increased by 0.1 volts every 45 seconds, up to 0.7 volts, where the program was terminated.

A Galvanostatic polarization curve on Labview was then performed. The current from the 0.2 ampere step in the Potentiostatic control was set as the region II upper limit, and a third of that value was set to the region I upper limit. The values of the differential current I and II were set to 0.01 amps and 0.05 amps, respectfully. Wait time I and II were both set to 10 seconds. The program was run to completion. The program was terminated, and the alligator clips were disconnected from the cell housing.

An EZStat Pro was then hooked up to the cell housing. The EZStat Pro application was used to first measure the OCP for 10 seconds. Then, 50 current data points were measured every 30 seconds. Once completed, the program was terminated, and the EZ Stat was disconnected from the cell housing.

A Labview Potentiostat/Galvanostat, hooked up to a Labview 20A current booster, was attached to the cell housing. NOVA 1.10.1.9 was launched, and Galvanostatic impedance was run, gathering 25 data points at 10, 40, 100, 200, 300, 600, 800, and 1000 mAmps, respectfully. Once this data was collected, Nova was terminated and the hardware was disconnected from the cell housing.
CHAPTER 3: RESULTS AND DISCUSSION

3.1. Polarization Data

3.1.1 Conditioning Parameters

The platinum-platinum PAFC produced an OCP of 0.9070 volts with PA loadings of 0.368 mgcm$^{-2}$ on the cathode and 0.352 mgcm$^{-2}$ on the anode. In the conditioning, the highest current accepted was at 200 millivolts to protect the load box. The value for the current at this voltage was 1.950 amps, thus the region II limit was set to 1.9 amperes. A third of this value, 700 milliamps, was set as the region I limit.

The iron catalyst PAFC produced an OCP of 0.7250 V, with a catalyst loading of 2.49 mgcm$^{-2}$, a PA loading of 2.47 mgcm$^{-2}$ on the cathode, and 0.356 mgcm$^{-2}$ of PA on the anode. In the conditioning, the highest current accepted was at 200 millivolts, to protect the load box. The value for the current at this voltage was 0.010 amps, thus the region II limit was set to 0.01 amperes. A third of this value, 3 milliamps, was set as the region I limit. Table 3 shows the conditioning data for both PAFC MEAs.
Table 3: Conditioning Data for PAFCs

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current (Ampheres)</th>
<th>Voltage (V)</th>
<th>Current (Ampheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.300</td>
<td>0.6</td>
<td>0.000</td>
</tr>
<tr>
<td>0.5</td>
<td>0.509</td>
<td>0.5</td>
<td>0.000</td>
</tr>
<tr>
<td>0.4</td>
<td>1.104</td>
<td>0.4</td>
<td>0.002</td>
</tr>
<tr>
<td>0.3</td>
<td>1.534</td>
<td>0.3</td>
<td>0.002</td>
</tr>
<tr>
<td><strong>0.2</strong></td>
<td><strong>1.957</strong></td>
<td><strong>0.2</strong></td>
<td><strong>0.010</strong></td>
</tr>
<tr>
<td>0.1</td>
<td>2.280</td>
<td>0.1</td>
<td>0.019</td>
</tr>
</tbody>
</table>

The highlighted regions at 0.2 volts shows the chosen limit for the Galvanostatic polarization. The limit acts as a safety to prevent damage to both the cell and the load box.

The platinum-platinum PEMFC produced an OCP of 0.850 volts, with a Nafion loading of 1.25 mgcm$^{-2}$ on the cathode and 0.88 mgcm$^{-2}$ on the anode. The current at 200 millivolts was 8.57 amperes, so 8 amperes was the region II limit and 3 amperes was the region I limit.

The iron catalyst PEMFC produced an OCP of 0.7890 volts, with a catalyst loading of 2.61 mgcm$^2$, a Nafion loading of 1.17 mgcm$^{-2}$ on the cathode and 0.96 mgcm$^{-2}$ of Nafion on the anode. The current at 200 millivolts was 0.91 amperes, so 0.90 was the region II limit and 0.30 amperes was the region I limit. Table 4 shows the conditioning data for the PEMFCs.

Table 4: Conditioning Data for PEMFCs

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current (Ampheres)</th>
<th>Voltage (V)</th>
<th>Current (Ampheres)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>0.5</td>
<td>5.42</td>
<td>0.5</td>
<td>0.090</td>
</tr>
<tr>
<td>0.4</td>
<td>6.51</td>
<td>0.4</td>
<td>0.187</td>
</tr>
<tr>
<td>0.3</td>
<td>7.51</td>
<td>0.3</td>
<td>0.352</td>
</tr>
</tbody>
</table>

26
The highlighted regions at 0.2 volts shows the chosen limit for the Galvanostatic polarization. The limit acts as a safety to prevent damage to both the cell and the load box.

### 3.1.2. Polarization Curves

Polarization Curves were produced for each FC. The polarization curves for the platinum-platinum cells are shown in Figure 8, and the polarization curves for the Fe catalyst cells are shown in Figure 9.

**Figure 1:** Platinum-Platinum Polarization Data. The x-axis represents current density (A/cm²), and the y-axis represents potential (Volts). Notice the similarity between the two.
Figure 2: Iron Catalyst Polarization Data. The x-axis represents Current Density (A/cm$^2$) and the y-axis represents potential (Volts). Note the Absence of Iron Catalyst in Phosphoric Acid Data.

3.1.3 Power Curves

The current values were transformed into current density values by dividing the current by the area of the MEAs, 4.24 cm$^2$. This was then plotted against the power, or the current density times the potential. Figures 3 through 5 show the plots of platinum-platinum power and iron catalyst power, respectively.
Figure 3: A plot of Pt-Pt PA polarization along with power density. The maximum power obtained from the cell was just over 100 mW/cm\(^2\).
Figure 4: A plot of Pt-Pt PEM polarization along with power density. The maximum power obtained from the cell was just under 100 mW/cm$^2$.

Figure 5: A plot of Fe PEM polarization along with power. The maximum power obtained from the cell was just under 100 mW/cm$^2$. 
Looking at the power densities from Figures 3-5, both Pt-Pt cells put out about 100 mWatts/cm$^2$ of power. The iron PEM produced only 30 mWatts/cm$^2$ of power. Thus, the Pt-Pt cells produce 3.3 times as much power per cm$^2$ as the iron catalyst cell produce.

The iron PAFC is an interesting case. The phosphoric acid did not work well with the iron catalyst. The theory behind this is the phosphoric acid was somehow inhibiting, or poisoning the iron catalyst, thus generating no measurable data. Originally, the theory was that the phosphoric acid was poisoning Pt, but the Pt-Pt PAFC performed fine, so this was rejected.

3.2 Impedance Data

3.2.1 Impedance Plots

Each FC produced a unique spectrum when analyzed by EIS. Figures 6 - 9 show the EIS spectra for each fuel cell analyzed.
Figure 6: Platinum-Platinum PEM EIS Data. Each curve is the Impedance measured at a different potential, from 10 mAmps (widest peak) to 1000mAmps (most narrow peak).

Figure 7: Platinum-Platinum PA EIS Data. Each curve is the Impedance measured at a different potential, from 10mAmps (widest peak) to 1000mAmps (most narrow peak).
Figure 8: Iron PEM EIS Data. Each curve is the Impedance measured at a different potential, from 10mAmps (widest peak) to 1000mAmps (most narrow peak).

Figure 9: Fe PA EIS Data. Each curve is the Impedance measured at a different potential, from 10mAmps (widest peak) to 1000mAmps (most narrow peak).
3.2.2 *Impedance Analysis*

Figure 6 represents Pt-Pt PEM EIS data. The data at each current range resembles a single arc, or kinetic loop. This data can be modeled by a Randalls cell [23]. This one loop feature is an indication that the process is being driven by the kinetics of oxygen reduction.

In Figure 7, the Pt-Pt PAFC data, cannot be modeled by a Randalls cell. The EIS exhibits a double loop. This feature relates to a charge transfer, at the higher frequency loop, and a mass transfer loop, at the low frequency loop. Figure 10 is an expansion of just one of the curves from figure 7. The two peaks are clearly evident, indicated both processes are taking place [23].

![EIS Graph](image.png)

**Figure 10**: A close view at one of the EIS graph lines. There is a clear loop in the low frequency zone, as well as a second loop in the higher frequency zone. The low frequency loop relates to mass transfer and the high frequency loop relates to the charge transfer. [23]
A circle graph was fit to each spectrum to model the number of loops, and thus upon analysis of each spectrum, in comparison to the Randalls cell model, it is evident that all cells, excluding the Fe PAFC, exhibit the Randalls cell model to some degree. The Pt-Pt PEMFC follows the Randalls cell to the definition, whereas the PT-PT PAFC and the non-PGM PEMFC show different charge and mass transfer areas. The non-PGM PAFC also exhibits the double loop feature, even though the cell produced no viable data in the polarization. This indicates that there is also Randalls cell deviation in the non-PGM PAFC.

Figure 11: An example of the circle fit from the Pt-Pt PEM cell. The circle Encompasses the whole of the data.
CHAPTER 4: CONCLUSION

The Pt-Pt cells were found to produce more power than the Fe-Pt, which was detailed from the power density plots. In the modeling comparison, all cells, excluding the Pt-Pt PEMFC, deviated from the Randalls cell model, indicating the different rates of charge transfer and mass transfer. This experiment has been applied to compare the Pt-Pt cell and the non-PGM cell with an iron catalyst. This is not the end of the potential research.

More catalysts can be tested in both PEMFCs and PAFCs. A different ionomer can be used, as well as different electrode material and ink compositions. With such a study as this one, there are many different variables that can be changed to acquire even more data. A study such as this could keep going. As new technologies and new catalysts arise, more data and research can and should be performed to find efficient catalysts that are cost effective and durable.
CHAPTER 5: REFERENCES


