DIAGNOSIS OF THE EFFECTS OF THERMAL CYCLING ON PEMFCS VIA ELECROCHEMICAL IMPEDANCE SPECTROSCOPY

by

ROBERT MICHAEL CONNELL

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Abstract

A new method of applying electrochemical impedance spectroscopy (EIS) as a diagnostic tool was used to investigate the effects of thermal cycling on proton exchange membrane fuel cells. The focus of this thesis was the generation of hardware required to accomplish this goal. Unlike previous work, this study used a specialized load bank to draw the periodic current necessary for impedance measurements.

This study also required the design and construction of new hardware to allow accelerated cycling of a single cell between ambient and operational temperatures. The equipment was tested (through experimentation) both to verify its functionality and to serve as a roadmap for a more thorough investigation into the effects of thermal cycling. It was hypothesized that cumulative damage due to thermal cycling would correspond to changes in cell impedance that were observable in characteristic frequency ranges.

The equipment was used to perform galvanostatic impedance measurements *in situ*. Measurements were made at four different current densities (0.2, 0.4, 0.6, and $0.8A/cm^2$) over the frequency range 1 to $1x10^6$ Hz. Cell temperatures were cycled between $20-80^{\circ}C$ or $30-90^{\circ}C$ at a rate of 1°C per second for up to 2000 cycles. The recorded data represents the first reported measurements covering these ranges.

The measured spectra were repeatable, produced results consistent with previous work and were as accurate as impedance measurements made using the traditional setup. Observed changes in impedance spectra as a function of thermal cycling were relatively minor but significant changes in impedance magnitude between 10 and 1000 Hz and changes in phase angle at frequencies greater than 10 kHz were measured.

The effects of thermal cycling on MEA performance were minor with no irrecoverable damage recorded at moderate stack pressures of 120 PSI and degradation rates below 0.057mV/cycle at increased stack pressure of 350 PSI. These results suggest that stack sealing pressure is a factor in thermal degradation and is an avenue for continued investigation.

Experimental data suggests that the main failure mode of thermal cycling is the formation of a contact resistance between the bipolar plates and current collectors due to degradation of the graphite. The contact resistance grew as large as $2x10^{-4} \ \Omega \text{ cm}^2$, leading to a potential drop of 0.25V, but available data was insufficient to calculate a growth rate.

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List of Symbols

α	Exchange transfer coefficient	
Ε	Electrical potential	V
$ ilde{E}$	Complex potential	V
E'	Real component of complex potential	V
E"	Imaginary component of complex potential	V
Ecell	Realized fuel cell potential	V
E^{o}_{rev}	Reversible fuel cell potential at standard temperature and pressure (STP)V
Erev	Reversible fuel cell potential	V
E_T	Thermal Voltage	V
$\dot{E^{o}}_{th}$	Thermoneutral potential at STP	V
E_{th}	Thermoneutral potential	V
F	Faraday's Constant	9.6485x10 ⁵ C/mol
ΔG	Gibbs free energy	J/mol
ΔG^{o}	Gibbs free energy at STP	J/mol
ΛG^0	Gibbs free energy of formation	J/mol
ΛH°	Enthalpy at STP	J/mol
$\Delta H^0 c$	Enthalpy of formation	J/mol
ΔΗ	Enthalpy change	J/mol
I	Current	A
i	Current density	A/cm ²
j i'	Real component of complex current density	A/cm ²
i"	Imaginary component of complex current density	A/cm ²
j İm	Internal current density	A/cm ²
jin İı	Limiting current density	A/cm ²
j. i.	Exchange current density	A/cm ²
n	Number of electrons per mole	
nast	Activation polarization	V
η_{aci}	Carnot efficiency	
n_c	Fuel utilization efficiency	
າ) ກຸ	Obmic polarization	V
η <i>onn</i> η	Operational fuel cell efficiency	
η_{op}	Concentration polarization	V
η_{pot} η_{nont}	Real fuel cell efficiency	
n real	Reversible fuel cell efficiency	
ANI	Change in number of moles of gas	
Δινg	Dhase angle difference between current and notential	degrees
ט ת	Program	Pa
P	Pressure	Pa
p_x	Logi input into a heat engine	тта Т
q_I	Gog Constant	8 3144 I/Kmol
ĸ		
κ_{Ω}	Snunt resistance	
R _{mem}	Membrane resistance	Ω
ΔS	Entropy change	J/mol

ΔS^{o}	Entropy of formation	J/mol
T	Temperature	K
T_{c}	Temperature of heat removal from a heat engine	K
T_{U}	Temperature at which heat is input into a heat engine	K
V	Voltage difference across the stack	V
V stack	Voltage difference across shunt resistor	V
• shun	Angular frequency	rad/s
ш 147	Work	J
W.	Electrical Work	J
7	Impedance	$\ldots \Omega cm^2$
2 7'	Real component of complex impedance	$\dots \Omega cm^2$
Z. 7"	Imaginary component of complex impedance	Ωcm^2
L	imaginary component of complex impedance	

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Chapter 1: Introduction

1.1 Societal Motivation

This thesis describes new approaches to accelerate and diagnose the effects of thermal cycling on proton exchange membrane fuel cells (PEMFCs). The research was focused on specific technologies and techniques but was motivated by widespread cultural, political, and economic factors.

The 20th century marked giant leaps in terms of technology, globalization, and population. Increases in transportation, industry, and communications have generated an increased demand for energy. Of particular concern is our current dependence on fossil fuels, which lead to well-documented adverse effects on the environment. Fossil fuel emissions lead to poor air quality, regional acidification, and increased atmospheric concentrations of greenhouse gasses (GHGs). These pollutants can lead to climate change ⁽¹⁾.

While adverse local atmospheric effects have been well documented, changes in global climate patterns due to GHG emissions are subject to intense debate. The most recent report from the Intergovernmental Panel on Climate Change suggests that small increases in global temperatures could alter crop yields, raise sea levels, change precipitation patterns, and increase the frequency of hurricanes⁽¹⁾.

To help promote the reduction of GHG emissions, an international agreement on prevention of climate change was reached in Kyoto in 1997. Ratified in 2002, industrialized countries (including Russia and with the notable exception of the United States) have agreed to reduce GHG emissions to an average of 6% below 1990 levels between 2008 and 2012. However, for these proposed changes to be effective, alternative energy systems that reduce dependence on fossil fuels must be developed.

1.2 Hydrogen and Electricity

Renewable energy sources, such as solar and wind power, are one way to reduce fossil fuel dependence. However, solar power is not currently economically viable as a large-scale energy producer and neither solar nor wind power produce energy continuously. Additionally, electricity is not efficiently stored in large quantities⁽²⁾ making it impractical for services requiring autonomous mobile power (i.e. transportation). Such services require a chemical feedstock to meet their demands.

Hydrogen can alleviate both of these problems. The use of electrolyzers to generate hydrogen would allow renewable energy sources to store a fraction of the energy produced. The hydrogen can then be used to generate electricity when the primary source is unavailable, or as fuel for mobile applications. The use of hydrogen as an effective storage medium for electrical energy allows renewable sources to penetrate energy sectors that are currently dominated by fossil fuels.

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1.3 Fuel Cell Types

Fuel cells can be differentiated by their ionic conductor, operating temperature, and type of fuel used. Beyond PEMFCs, the most common types are Solid Oxide (SOFC), Direct Methanol (DMFC), Molten Carbonate (MCFC), Alkaline (AFC), and Phosphoric Acid (PAFC) fuel cells. A brief synopsis of each including advantages and disadvantages is provided in table 1.1.

	Fuel	Temperature	Applications	Advantages	Disadvantages
PEMFC	Hydrogen	70-90°C	Mobile & Portable Power	high power densities proven long life operation	CO intolerance, water/heat mgmt, expensive catalyst
DMFC	Methanol	60-90°C	Mobile & Portable Power no need for fuel reforming, compression, or humidification		Fuel Crossover, complex stack structure
SOFC	Hydrocarbons or hydrogen	800-1000°C	Power Generation	Internal reforming, well suited for co-generation, CO tolerant	high operating temp, high cost
MCFC	Hydrocarbons	550-1000°C	Power Generation internal reforming, high efficiency		unstable electrolyte, undetermined lifetime
AFC	Hydrogen	70-90°C	Space and terrestrial transport	Inexpensive materials, faster kinetics, CO tolerance	CO2 intolerant low efficiency
PAFC	Hydrogen	150-210°C	Power Generation	commercially available	liquid electrolyte

Table 1.1: Fuel Cell Properties

This study focuses on PEMFCs. As such, the analysis focuses on fuel cells that use hydrogen as a fuel and protons as the ionic species. However, it should be noted that the proposed diagnostic techniques could be applied to examine the effects of thermal cycling in all fuel cell types listed above.

1.4 Fuel Cell Applications

Fuel cells are electrochemical devices that combine fuel and oxidant in a non-combustion process to generate electricity. When hydrogen is used as a fuel, the only waste products are water and heat. Some types of fuel cells can use other fuels such as natural gas or methanol. In doing so, pollutants such as CO, NO_x , and particulates are greatly reduced compared to combustion of the same fuels. Additionally, by converting chemical energy directly into electrical power, fuel cells avoid intermediate losses associated with conversion into heat and mechanical energy, leading to higher efficiencies. These benefits can be realized in a number of applications including:

- portable power
- power generation
- mobile power

1.4.1 Portable Power

Applications with power demands of 1kW and below are likely the first area for widespread market penetration. The reason is that fuel cells in this range can compete economically with batteries, the incumbent technology⁽³⁾. Examples of these applications include portable electronics, communications, remote sensors, power tools, and many recreational devices.



Figure 1.1: Commercial applications – Ballard Airgen (left) and DMFC powered phone (right)

Some products are already commercially available, such as Ballard Power's Airgen unit shown in shown in figure 1.1. The 1.2 kW Airgen is marketed as a silent, indoor alternative to diesel or gasoline generators. Electronics companies such as Motorola are looking to DMFCs to power electronic devices such as cell phones and laptops.

1.4.2 Large-scale Power Generation

Current trends in power generation show a move from the centralized model of the 1980s towards distributed power generation ⁽⁴⁾. This marks a move away from a few plants with large capacities (>10MW) to a distributed system with many smaller plants. Current fuel cell plants are designed in the range of a few hundred kilowatts to a few megawatts.

Companies such as Ballard Power Systems are pursuing PEMFC power plants. However, high temperature SOFCs, with their high efficiency and ability to accept a wide variety of fuels offer the best option for this type of application. These fuel cells can be used alone or in co-generation with gas turbines. Figure 1.2 shows a 300kW Siemens-Westinghouse combined cycle plant. Such combined cycle systems have theoretical efficiencies over 80% and are expected to have operational efficiencies of 75% when operated on natural gas and 60% when operated on coalderived gas ⁽⁵⁾.



Figure 1.2: SOFC Co-generation Plant

1.4.3 Mobile Power

Much of the fuel cell media attention has been directed towards the promise of fuel cell powered vehicles (FCVs). The possibility of zero tailpipe emissions would help reduce pollution in urban areas and hydrogen-powered vehicles would be a major step towards reducing fossil fuel dependence. The technology to build PEMFC powered vehicles exists and most major automotive companies have prototype and demonstration FCVs. For example, a demonstration fleet of four Ford Focus FCVs (figure 1.3) will operate in Vancouver as part of British Columbia's Hydrogen Highway program.



Figure 1.3: Ford Focus FCV

However, before fuel cell powered vehicles become widely available two major hurdles must be overcome. Primarily, the technology is still too expensive. Even at mass-production volume, the cost of a FCV is still an order of magnitude higher than an equivalent vehicle with an internal combustion engine ⁽⁶⁾. Secondly, there is not currently a widespread hydrogen-fueling infrastructure in place. A reliable means of generating and distributing hydrogen will be central to the proliferation of FCVs.

Until these problems are overcome, fuel cells will be restricted to powering niche market vehicles where they provide an economic advantage. Examples of this include forklifts and utility vehicles, which can eliminate costly battery recharging bays and golf course grooming equipment which, when powered by quieter fuel cells, allows the courses to begin grooming earlier without violating noise bylaws.

1.5 Motivation and Contributions to the field

Before fuel cells can reach consumer markets, they must become more robust and reliable. Central to this goal is the identification of mechanisms responsible for fuel cell failure so that their design can be modified to mitigate the effects. Additionally, once the failure modes are identified, diagnostic techniques must be developed to alert system operators to the cause of performance degradation and allow corrective action to be taken before catastrophic failure occurs.

Electrochemical Impedance Spectroscopy (EIS) is a diagnostic technique especially well suited for fuel cell systems. In an EIS measurement, a periodic alternating current (AC) load is superimposed on a constant or slowly varying linear direct current (DC) load. A comparison between the measured response and the applied stimulus yields the system's electrochemical impedance at a specific AC frequency. Typically the measurement is done for a spectrum of frequencies ranging from millihertz to megahertz.

Several groups have used EIS to characterize performance of PEMFCs ⁽⁷⁻¹¹⁾ and it was recently used by Mérida et al. to diagnose such failure modes as cell flooding and dehydration ⁽¹²⁾. The focus of this thesis was the generation of new hardware required to allow the diagnosis of thermal cycling by EIS. A new method of applying EIS was used and the following contributions are made to the field.

This study represents the first reported instance of EIS being applied using a separate AC load bank. This is an important step towards making EIS a practical diagnostic tool and moving it from the laboratory towards real applications. Since the required equipment was not commercially available, a specialized load bank was designed and built for this study. New hardware to allow accelerated thermal cycling of a single PEMFC cell was also developed and data gathered represents the first reported set of EIS measurements for thermal degradation in the temperature and frequency ranges used.

1.6 Chapter Summary

Chapter 2 of this thesis deals with PEMFC performance indicators and failure modes. Chapter 3 presents the advantages and disadvantages of current diagnostic techniques while Chapter 4 examines EIS in detail. Chapter 5 details the hardware built and assembled for this study. Chapter 6 describes the experimental techniques used and Chapter 7 presents the gathered data and discusses the results. Conclusions and recommendations are presented in Chapter 8.

Chapter 2: Theoretical Background

2.1 Thermodynamics and Electrochemistry

2.1.1 Principle of Operation

The basic structure of a PEMFC consists of two electrodes, an anode and a cathode, separated by an ionic conductor. The ionic conductor must be permeable to hydronium ions and have low electronic conductivity and gas permeability. The porous electrodes are permeable to gasses and liquids, and are connected to an electrical circuit as shown in Figure 2.1. The assembly is powered by hydrogen at the anode and oxidant (typically oxygen, either pure or from air) at the cathode.



Figure 2.1: Fuel Cell Schematic

During operation, hydrogen molecules are oxidized and dissociated at the anode. The resulting electrons flow through an external circuit and can be used to drive an electrical load. The circuit is completed by a current of equal magnitude through the ionic conductor. At the cathode, the electrons reduce the oxygen molecules, which combine with available protons to form the product water. At standard temperature and pressure of 25° C and 1atm, the anode and cathode reactions are:

anode :
$$H_2(g) \rightarrow 2H^+ + 2e^-$$
 (2.1)
cathode : $\frac{1}{2}O_2(g) + 2H^+ + 2e^- \rightarrow H_2O(l)$
 $\Delta H^\circ = -285 \text{ kJ/mol}$
 $\Delta G^\circ = -237 \text{ kJ/mol}$

2.1.2 Heat Engine Efficiency

The overall net reaction in equation 2.1 is identical to what would occur in a combustion process involving hydrogen and oxygen. However, work obtained from combustion processes is limited

by the Carnot efficiency (η_c) of an ideal heat engine (the term heat engine includes steam and gas turbines as well as the internal combustion engine).

$$\eta_c = \frac{w}{q_1} = \frac{T_H - T_C}{T_H}$$
(2.2)

The ratio of work (w) to input heat (q_1) in equation 2.2 is maximized by increasing the temperature (T_H) at which input heat is transferred into the system or decreasing the temperature at which it exits (T_C) . If heat is generated by a chemical reaction, q_1 can be equated to the enthalpy change (i.e. heat produced in an isobaric reaction).

$$q_1 = -\Delta H_{rxn} \tag{2.3}$$

Clearly, high efficiencies can only be obtained when the temperature difference is large (i.e. when $T_H \rightarrow \infty$, or $T_C \rightarrow 0$). Practically, the upper service temperature of real materials limits this temperature difference and heat engine efficiencies are rarely above 50% (exceptions are combined cycle and large reciprocating engines).

2.1.3 Electrical Efficiency

For a reversible (ideal) electrochemical system, the maximum work that can be obtained corresponds to the change in Gibbs free energy (see appendix A):

$$w_e = -\Delta G \tag{2.4}$$

Denoting the fuel cell potential as E, the work associated with moving electrical charge is simply $w_e = nEF$, where F is Faraday's constant. For the reaction in equation 2.1, each mole of hydrogen consumed will produce two electrons. Therefore, the reversible PEMFC potential is given by

$$E_{rev}^{o} = \frac{-\Delta G_{f}^{o}}{2F}$$
(2.5)

For liquid water, ΔG_f^{o} is -2.37×10^5 kJ/mol, which gives an ideal voltage of 1.229V. The thermoneutral potential (E_{th}^{o}) is defined as the ideal cell potential if the entire enthalpy of formation was available as work.

$$E^{o}_{th} = \frac{-\Delta H^{o}_{f}}{2F}$$
(2.6)

For the HHV of hydrogen at standard conditions, ΔH_f^0 equals -2.86x10⁵ kJ/mol, this represents a potential of 1.482V. Equations 2.5 and 2.6 can be rearranged to provide an expression for reversible cell efficiency (η_{rev})

$$\eta_{rev} = \frac{E_{rev}^o}{E_{th}^o} = \frac{\Delta G_f^o}{\Delta H_f^o} = 1 - \frac{T\Delta S_f^o}{\Delta H_f^o}$$
(2.7)

Inspection of equation 2.7 shows that reversible fuel cell efficiencies drop as temperature increases. This contrasts with heat engine efficiencies, which increase at higher temperatures. Efficiencies of an ideal heat engine and reversible fuel cell are shown in figure 2.2 along with the melting temperatures of common engineering materials.



Figure 2.2: Efficiencies of fuel fells and heat engines vs. temperature

It can be seen that ideal fuel cells have higher efficiencies than heat engines at temperatures below $800^{\circ}C^{(13)}$. While this would suggest better fuel cell performance at lower temperatures, the practical losses discussed later in this chapter are reduced at higher temperatures. For practical PEMFCs, optimal efficiency occurs in the range of $60-80^{\circ}C$.

In practice, the cell potential, $E_{cell}(j)$, is a function of current density, cell temperature, and stack pressure. The most significant factor is current density and potential drops as cell loading increases. This leads to an operational efficiency (η_{op}) given by

$$\eta_{op} = \frac{E_{cell}(j, T, P)}{E_{rev}^o}$$
(2.8)

Additionally, not all of the fuel that passes through the cell is used in the reaction. The fuel utilization efficiency, can be defined as:

$$\eta_f = \frac{\text{mass of fuel reacted in cell}}{\text{mass of fuel input to cell}}$$
(2.9)

Real efficiency can then be defined as the product of the reversible, operational, and fuel utilization efficiency:

$$\eta_{real} = \eta_{rev}\eta_{op}\eta_f = \left(\frac{\Delta G(T,P)}{\Delta H(T,P)}\right) \left(\frac{E_{cell}(j,T,P)}{E_{rev}(T,P)}\right) \eta_f = \left(\frac{E_{rev}(T,P)}{E_{th}(T,P)}\right) \left(\frac{E_{cell}(j,T,P)}{E_{th}(T,P)}\right) \eta_f = \frac{E_{cell}(j,T,P)}{E_{th}(T,P)} \eta_f \quad (2.10)$$

Note that this does not include efficiency losses due to parasitic loads required for reactant conditioning such as humidification, pressurization, etc.

2.1.4 Effects of Temperature and Pressure

The reversible cell potential from equation 2.5 is obtained at standard conditions of 25° C and 1 bar of pressure. To find the reversible cell potential at other temperatures and pressures one must apply the Nernst equation. For hydrogen and oxygen, the reversible cell potential at non-standard temperature and pressure can be found by

$$E_{rev} = E_{rev}^{o} + \frac{RT}{2F} \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right)$$
(2.11)

To find specifically how cell potential changes with temperature at constant pressure, we can apply the thermodynamic identity

$$\left(\frac{\partial E}{\partial T}\right)_{\nu} = \frac{\Delta S}{nF} \tag{2.12}$$

which leads to

$$E_{rev}(T) = E_{298}^0 + \frac{\Delta S}{2F}(T - 298)$$
(2.13)

Since ΔS decreases with increasing temperature, this once again shows that reversible cell potential is reduced at higher temperatures. The change of potential with pressure at constant temperature is found by applying the identity

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{-\Delta N_g}{nF} \tag{2.14}$$

where ΔN_g represents a volume change caused by the state (liquid, gas, etc.) of the reactants and products. Referring to equation 2.1, ΔN_g is found as the number of moles of products in a gaseous state subtract the number of moles of gaseous reactants. Therefore,

$$E_{rev}(P) = E_{1atm}^o - \frac{\Delta N_g RT}{2F} \ln P$$
(2.15)

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where P is measured in atmospheres. Regardless of whether product water is in liquid or gaseous form, there will always be more moles of gaseous reactants than products. Hence, cell potential will increase as pressure increases.

2.2 Real Operating Potentials

Cell potentials achieved during operation will always be smaller than E^{o}_{rev} . There are four categories of associated losses:

- Activation polarization
- Ohmic polarization
- Concentration polarization
- Reactant crossover

The voltage drop resulting from each of these losses is called an overpotential.

2.2.1 Activation Polarization

Activation polarization losses are associated with slow reaction rates at the surface of the electrodes. With chemical reactions, slow kinetics result from activation energies that can be reduced by increasing a driving force such as pressure or temperature. Electric potential is a similar driving force and the extra voltage required to overcome slow kinetics can be approximated by

$$\eta_{act} = \frac{RT}{\alpha nF} \ln\left(\frac{j}{j_o}\right)$$
(2.16)

where α is the *exchange transfer coefficient*, which ranges between 0 and 1 and is approximately 0.5 for PEMFCs. The *exchange current density*, j_o , is representative of the effectiveness of the electrode material. A large j_o value is representative of a more active catalyst and corresponds with lower activation losses.

Increases in activation polarization are usually associated with loss of apparent catalytic activity. Degradation modes include catalyst ripening, crystallite migration, sintering, and agglomeration⁽¹⁴⁾.

2.2.2 Ohmic Polarization

These losses correspond to resistance to ion flow through the membrane and are found by the equation

$$\eta_{ohm} = IR_{mem} \tag{2.17}$$

It can be seen that the ohmic losses are directly proportional to the load, *I*, drawn by the cell. At constant load, an increase in ohmic polarization is caused by increasing membrane resistance, $R_{mem.}$ Factors known to increase ohmic losses include time, exposure to contaminants, thermal and hydration cycling, and membrane dehydration ⁽¹⁴⁾.

2.2.3 Concentration Polarization

As reactants are consumed during operation, there will be a decrease in concentration near the electrode. The extent of the decrease depends primarily on the current density drawn from the cell as well as physical factors determining how fast reactants can be replenished. Reduced concentration results in a decrease in the local partial pressure of the reactants. This leads to a voltage drop that can be approximated by

$$\eta_{conc} = \frac{RT}{2F} \ln \left(1 - \frac{j}{j_L} \right)$$
(2.18)

The *limiting current density* (j_L) occurs when reactants are consumed at a rate equal to their maximum supply speed. In this situation the local partial pressure approaches zero and the concentration losses become severe. Factors that impede reactants from being consumed will increase concentration polarization. These include cell flooding and delamination of the MEA.

2.2.4 Reactant Crossover and Internal Currents

These are losses resulting from fuel and electrons crossing the membrane. Reactant crossover creates an internal current (j_{in}) that is not measured. In PEMFCs this internal current is typically in the range of 2-3 mA/cm² and modifies equation 2.16 as such:

$$\eta_{act} = \frac{RT}{\alpha nF} \ln \left(\frac{j + j_{in}}{j_o} \right)$$
(2.19)

Since operational currents are typically hundreds of milliamps per square centimeter, reactant crossover has a negligible effect under operational conditions. However, even a few milliamps of internal current can result in a significant activation polarization and explains why open circuit voltages are often 0.2-0.3V lower than the 1.23V ideal ⁽¹³⁾.

2.2.5 The Polarization Curve

A polarization curve is a plot of cell potential versus current density. This is a common method of characterizing fuel cell performance. Shown in figure 2.3, the polarization curve demonstrates how each of the aforementioned polarizations is manifested.

Activation polarization occurs at low current density and results in a sharp initial drop in potential. The ohmic polarization varies proportionally with current drawn and is responsible for the linear drop at moderate current densities. Concentration polarization dominates at high loads causing a rapid voltage drop as the limiting current density is approached.



Figure 2.3: The Polarization Curve

2.2.6 Empirical Equations

While equations 2.15 - 2.18 are useful for defining the polarization curve; they neglect practical factors such as electrode roughness, membrane dehydration, catalyst loading, etc. As such, fuel cell performance is usually modeled using empirical equations. For example, Kim and Srinivasan have developed the following model to fit experimental data ⁽¹⁵⁾:

$$E_{cell} = E_{rev} - b \log\left(\frac{i}{i_0}\right) - iR_c - me^{ni}$$
(2.20)

Where the factors b, R, m, and n can be found from tables similar to table 2.1.

Oxidant	T (oC)	P (atm)	Eo (mV)	b (mV/dec)	$R(\Omega cm^2)$	m (mV)	n (cm2 mA-1)
	50	1	943.00000	62.00000	0.36300	0.38000	0.01030
	50	3	978.00000	60.00000	0.36300	2.90000	0.00572
AIR	50	5	991.00000	57.00000	0.40600	3.08000	0.00559
,	70	1	943.00000	62.00000	0.23800	3.75000	0.00638
	70	3	982.00000	59.00000	0.30600	36.00000	0.00653
	70	5	1000.00000	57.00000	0.28000	5.20000	0.00361
	50	1	979.00000	62.00000	0.30000	21.50000	0.00217
	50	3	1010.00000	64.00000	0.31300	3.40000	0.00321
0-	50	5	1027.00000	63.00000	0.29800	4.63000	0.00305
02	70	1	970.00000	60.00000	0.25900	12.50000	0.00210
	70	3	1024.00000	63.00000	0.23100	10.10000	0.00200
1	70	5	1032.00000	54.00000	0.24200	25.70000	0.00145

Table 2.1: Reference factors for the empirical model developed by Kim and Srinivasan⁽¹⁵⁾

2.3 Fuel Cell Failure

PEMFCs are power generation devices in that they produce electrical power when provided with both fuel and oxidants as reactant. Therefore, outright PEMFC failure would be defined as the inability of the stack to produce power in the presence of proper reactants. However, failure can also be defined to have occurred if the stack cannot provide sufficient power to its application, or meet specific operational demands such as fuel efficiency, voltage output, acceptable exhaust emissions, timely power delivery, or power production under specific environmental conditions such as low-temperature startup. Fowler *et. al* ⁽¹⁴⁾ define the term *available* for a fuel cell stack that is meeting the following application-specific conditions.

- **Power Capacity** the stack must provide a minimum net power output at all times to satisfy application demands
- Voltage Output Range most applications require power within a specific voltage range. This limits the areas along the polarization curve where the stack can be operated.
- **Fuel Efficiency** measures net electrical power output from the stack against the available chemical energy in the fuel based on the lower heating value (LHV).
- Emission Profile allowable emissions of air pollutants such as SO_x, NO_x, and particulate matter cannot be exceeded.
- **Response Time** defined as the amount of time needed to provide full power from idle conditions (or vice versa). An important parameter in both transportation and back-up power generation applications.

Therefore, a PEMFC stack that does not meet one or more of the previous conditions would be considered unavailable and can be considered to have failed even though it still produces electrical power.

Due to the unstable and reactive nature of the MEA, voltage output tends to degrade over time at a constant rate. Laboratory results to determine this rate have varied depending on setup but range between 2-60 μ V/h with most rates below 10 μ V/h⁽¹⁴⁾. Performance degradation at higher rates is indicative of a problem. An understanding of fuel cell failure modes is essential towards designing appropriate diagnostic techniques.

2.4 Failure Modes

The purpose of this study was to examine the effects of thermal cycling on PEMFC performance. In order to make the results as accurate as possible, it was important to minimize the effects of concurrent mechanisms causing damage to the cell. In a laboratory setting, some failure modes, such as catalyst poisoning, can be avoided. Others, such as reactant contamination can be managed. This section examines relevant failure modes and techniques used in this study to mitigate their effects.

2.4.1 Catalyst poisoning (commonly from CO)

In PEMFCs, the oxidation of fuel at the anode and reduction at the cathode depend on the presence of a catalyst. Currently platinum is used to catalyze these reactions. Catalyst poisoning due to outside contaminants is a major cause of fuel cell failure. The most common cause of contamination is due to CO in the fuel stream ⁽¹⁶⁾.

CO is commonly found in the fuel stream if a reformate fuel is used as opposed to pure hydrogen⁽¹⁷⁾. CO levels as low as 10ppm can cause significant adsorption to the platinum surface and can seriously degrade fuel cell performance. An endurance test study by Mitsuda et al ⁽¹⁸⁾ using simulated methanol reformate fuel (75%H₂, 25%CO₂, 100 ppm CO) found voltage degradation of 40μ V/h, or 10 times the degradation rate when pure hydrogen was used.

Outside of the laboratory, contamination of the oxidant stream will also be a practical issue. PEM powered vehicles sharing the road with conventional vehicles will unavoidably experience combustion exhaust products entering the air inlet ⁽¹⁹⁾. These contaminants include CO_2 , CO, unburned hydrocarbons, and sulfur compounds. However, in this study, the use of high purity bottled hydrogen as a fuel and filtered compressed air as an oxidant ensures that no poisonous substances are found in the gas streams.

2.4.2 Metal ion Contamination

Another source of contaminants is the corrosion of stack or balance of plant components. Corrosion products that make their way to the membrane or catalyst can lead to failure. Cations such as Na¹⁺, Ca²⁺, Fe³⁺, and Al³⁺ can exchange for sulfonite groups within the membrane; having a negative effect on proton conduction. However, effects are negligible until the contaminants build to a significant level ⁽²⁰⁾. Additionally, Cu²⁺ and Fe²⁺ have been shown to accelerate membrane degradation by a peroxide reaction.

These failure modes were minimized in two ways. Primarily, by using materials that did not leach contaminants, such as graphite and stainless steel, and by using high purity de-ionized (DI) water to help prevent contaminants from entering the cell. Secondly, contaminants must build up over time within the cell before they have a noticeable affect on performance ⁽²¹⁾. By keeping the runtime of the experiments in this study under 100 hours, any contaminants in the system did not have time to build up to detrimental levels.

2.4.3 Structural Component Failures

PEM fuel cell stack components are not generally subject to mechanical failure. The stresses within the stack are moderate and, since there are no moving parts, generally static. The components can easily be designed to pass shock and vibration testing ⁽²²⁾.

Other than the MEA, compressive seals are the only component subject to wear under normal operation. Over time, seals can oxidize or experience heat hardening within the stack ⁽¹⁴⁾. A faulty seal would at best be a hindrance on performance as leaking fuel or oxidant would not reach its intended destination. More likely, the leak would lead to catastrophic and dangerous failure within the fuel cell. Any leak that allows fuel and oxidant to mix in the presence of a catalyst will create a hot spot, quickly eroding the membrane or further damaging the seal. This leads to a larger leak and a larger hot spot that could extensively damage stack components. Vigilant leak testing was performed throughout experimentation to ensure seal integrity.

2.4.4 Membrane Dehydration

The NafionTM polymer in the membrane must be kept hydrated to work properly. Effects such as electro-osmotic drag and evaporation can remove water from the cell faster than it is generated. Membrane dehydration leads to dramatic changes in the polymer microstructure. Interconnecting channels that permit passage of the hydrated ions shrink, reducing the protonic mobility ⁽¹²⁾.

The increased resistance to protonic transport causes ohmic heating in local drying regions. This heating exacerbates the drying process and can lead to regions of complete membrane dry-out. In these extreme cases the local temperature can rise above the membrane's melting point and membrane integrity can be compromised. Under less severe conditions, membranes can recover from dehydration but performance will be reduced as the microstructure is cumulatively altered from each cycle.

The effects of dehydration are manifested as a steady voltage decline at constant load. The simple solution is to increase the amount of water in the inlet reactant streams. Careful management of the relative humidities of the inlet gas streams was used to ensure membrane hydration during testing.

2.4.5 Flooding

Humidification of the fuel and oxidant streams is the common method of preventing membrane dehydration. However, too much water can also be a problem. The presence of liquid water in the porous electrode layers can displace reactants from the active sites. Macroscopic water layers can block gas distribution channels cutting off entire sections of the fuel cell to reactants.

Large PEMFC applications can combat flooding by using long, serpentine paths in the flow fields. These paths require larger pressure drops to achieve necessary reactant flow rates, large enough to physically blow out water once it has blocked the flow field. The downside of this technique is the larger parasitic loads associated with more powerful compressors and blowers.

In such situations, frequent and dramatic drops in voltage are observed as active sites are blocked by liquid water. A voltage recovery is then seen when the water is blown out and the active sites are once again available.

For less severe flooding, some of the active sites can be blocked without enough liquid water present to flood the channel and produce a telltale blowout. In this case, one way to test for cell flooding is to increase the cathode flow rate. This increases the amount of evaporation on the cathode and, if the cell is flooding, will result in a voltage increase as more active sites are made available. If the cell is not flooding, the increased evaporation will lead to dehydration and a voltage decrease will be observed. This test was used frequently to ensure that neither flooding nor dehydration occurred during testing.

2.5 Thermal Cycling

The cumulative negative effects of thermal cycling are inevitable for most fuel cell systems. Fuel cells used for large-scale power generation can avoid changes in temperature by running continuously under constant load during normal operation. However, for mobile and portable applications it is impractical to either run the fuel cells continuously or use an outside heat source to maintain temperature.

PEMFCs in these applications will cycle between operational temperatures of $60-90^{\circ}$ C and ambient environmental temperatures between -30 and 30° C when not in service (see figure 2.4).



Figure 2.4: Thermal Cycle between 20°C and 80°C

2.5.1 Previous Work on Thermal Cycling

Several groups have studied the effects of thermal cycling on PEMFCs. Many of the studies have focused on the effect of freezing water when ambient temperatures are below zero degrees Celsius ⁽²³⁻²⁶⁾. Others have reported performance degradation measured in experimental stacks for thermal cycling involving non-freezing conditions ⁽²⁷⁻³⁰⁾. In all cases, the results have varied widely depending on temperature range cycled and MEA used. The results are summarized in table 2.2

Group	Membrane	Temperature Range (°C)	# Cycles	Average degradation (mV/cycle)
EunAe et al.	Nafion 115	80 to -10	4	25
	dehydrated Naf. 115	80 to -10	15	0.53
Wakizoe et al.	Aciplex-S1004	70 to -20	8	56.3
	Aciplex-S-BH	70 to -20	8	4.4
Wilkinson et al.	Nafion 112	63 to -30	33	<0.01
Giddey et al.	Nafion 112	60 to room temp	40	0.83
Sakamoto et al.	unspecified	80 to room temp	1000	0.05-0.09
Sishtla et al.	Nafion 112	60 to room temp	4	2.5

Table 2.2: Thermal Cycling Studies

Thermal cycling including freezing has been shown to have a dramatic effect on cell performance. EunAe et al. report a performance decrease of 25 mV/cycle over four cycles ⁽²³⁾. When steps were taken to dehydrate the cell before freezing, this degradation was reduced to 0.53 mV/cycle ⁽²⁴⁾. Wakizoe et al. examine the effects of thermal cycling between on a new membrane material ⁽²⁵⁾. The results were a performance decrease of 56.3 mV/cycle for Aciplex-S1004 and only 4.4mV/cycle for reinforced Aciplex-S-BH membranes. Conversely, work by Wilkinson and St-Pierre ⁽²⁶⁾ showed nearly no performance degradation in membranes cycled between 63°C and -30°C with a voltage loss of less than 0.01mV/cycle. Wilkinson attributed the robustness of the fuel cells in their experiments to an improved catalyst layer structure ⁽²⁷⁾.

For thermal cycling without the effects of freezing, the effects are more moderate. Giddey et al. report a performance decrease of $0.83 \text{mV/cycle}^{(28)}$. Sakamoto et al. encountered degradation at a rate of 0.05-0.09 mV/cycle over 1000 start-stop cycles between room temperature and 80°C ⁽²⁹⁾. Sishtla et al. found voltage drops of 2.5 mV/cycle over 4 cycles ⁽³⁰⁾. However, the 4 cycles were spread out over 1200 hours so the effects of degradation with time should be taken into account.

2.5.2 Damage Mechanisms of Thermal Cycling

The available information about the effects of thermal cycling on PEMFCs is limited. While the studies report the results of the thermal cycling, few conclusions are drawn as to the associated

mechanisms. For example, Giddey et al. cite possible reasons for the associated increase in ohmic resistance as: membrane degradation, increase in contact resistance between various stack components, some corrosion of the copper collector plates, deterioration of the catalyst, carbon paper, and diffusion layer ⁽²⁸⁾. EunAe et al. narrow this field slightly by saying that the increase in ohmic resistance is not attributable to the increase in proton conductivity of PEM, but probably due to an increase in the contact resistances between electrodes and PEM and between electrodes and the flow field ⁽²⁴⁾.

Work by Wakizoe with reinforced membranes states that membranes with higher *dimensional stability* are more resistant to the effects of thermal cycling. Cleghorn ⁽³¹⁾ confirms that dimensional stability is an important factor in MEA durability and Fowler states that dimensional cycling could result in electrode delamination ⁽¹⁴⁾.

This study is not concerned with the mechanisms by which thermal cycling damages PEMFCs so much as with changes in a diagnostic profile. The chosen diagnostic tool has been proven capable of showing which parts of the cell are affected by various failure modes ⁽¹²⁾ so information gathered from this study may help uncover the damage mechanisms of PEMFCs.

Chapter 3: Fuel Cell Diagnostics

With so many possible failure modes, it is not surprising that a wide variety of diagnostic techniques are used for fuel cells. These techniques can be broadly grouped into two categories. The first group involves intrusive techniques requiring that the fuel cell stop or alter its duty cycle to enter a diagnostic mode. The second group involves diagnostic techniques that can be used while the cell is operating without affecting the cell's duty cycle. These techniques are summarized in table 3.1 and explained in the following sections.

Diagnostic Technique	Description	Attractors / Barriers
Intrusive Techniques		
Current Interrupt	Stack load is suddenly disconnected and residual	Cheap, though it requires
	current is measured as a function of time. Ohmic	disconnection of stack load
	losses disappear immediately while other losses	
	have characteristic relaxationtimes	
Polarization Curve	Stack load is slowly increased over the full range	Requires a change of duty cycle
	of current drawn and corresponding potentials are	and not all loads are capable of
	measured and compared to baseline performance	drawing multiple current densities
Cyclic Voltametry	Gives information on catalytic activity and presence	Requires a change of gasses fed
	of contaminants. Requires that nitrogen be fed to	to anode and cathode
	the anode and hydrogen to the cathode for use in	
	full cell PEMFCs (24)	
Post-Mortem Analysis	When all else fails, pull the stack apart and	Thorough, though time consuming
	examine each piece individually	and expensive
X-Ray Fluorescence	A beam of X-Rays is directed at the MEA to scan	Requires visual access to MEA, so
Spectrometry (XRF)	for contaminants or other damage	partof a post-mortem analysis
Non-Intrusive Techniques		
DC Voltage Monitoring	Monitor stack potential at a given current density.	Commonly used but does not give
	A voltage drop is indicative of performance	source of perfromance drop
	degradation	
Pressure Drop Monitoring	Monitor stack pressure drop for rapid changes.	Cannot diagnose many failure
	Used to diagnose cell flooding or seal failure	modes such as dehydration or
		catalyst poisoning
Electrochemical Impedance	Cell impedance to a small AC load is measured.	Currently requires bulky and
Spectroscopy (EIS)	By varying the frequency of the AC load, different	expensive equipment
	aspects of cell behaviour can be analyzed	

 Table 3.1: Diagnostic Techniques

3.1 Intrusive Techniques

3.1.1 Current Interrupt

As the name suggests, current interrupt techniques involve a sudden disconnection of the current load. The cell potential is then measured as a function of time. Losses due to internal or ohmic resistance will disappear immediately. Other losses, such as charge dispersion in the double layer can be identified by a characteristic relaxation period. A major downside to the current interrupt method is that disconnecting the load is not always an option.

3.1.2 Polarization Curve

The polarization curve is a graph of voltage vs. current density for the cell or stack (see section 2.2.5). It is obtained by slowly increasing the current drawn from the cell and examining the associated voltage. As the cell incurs damage, it will generate less potential at a given current density. The polarization curve can be used to compare present performance against a baseline.

The polarization curve also provides information about whether performance losses are due to increased activation, ohmic, or concentration polarization. This technique is well suited to laboratory work with flexible load banks. However, real loads do not always lend themselves to being able to draw a wide range of currents necessary to produce a polarization curve.

3.1.3 Cyclic Voltammetry

Used to provide information about catalytic activity and the presence of contaminants. This technique is normally done using half-cells in the laboratory, however a full cell can be run in a special mode to create a reference and counter electrode. EunAe et al. do this by running nitrogen to the anode and hydrogen to the cathode of their cell ⁽²⁴⁾. To accomplish this, the cell is shut down, purged, and reconnected with new reactants. Clearly, this cannot be done while the cell is in normal operation.

3.1.4 Post Mortem Analysis

When all else fails, disassemble the stack and examine each component separately. Although thorough, this is a costly and time-consuming process and is preferably avoided.

3.1.5 X-Ray Fluorescence Spectrometry (XRF)

A beam of x-rays is directed at the MEA. Atoms struck by the x-rays may discharge electrons, resulting in an unstable condition. As the atoms stabilize they produce x-rays when outer shell electrons move inward to replace ejected electrons. Each element produces x-rays with a unique energy signature allowing researchers to determine what materials are present. This technique is used to scan the membrane for contaminants and other damage ⁽³²⁾. However, it requires direct visual access to the membrane therefore would be part of a post-mortem analysis.

3.2 Non-Intrusive Techniques

3.2.1 DC Voltage Monitoring

Cell potential is a commonly used indicator of performance in fuel cell stacks. A drop in cell potential at a given current loading is an indication of performance degradation. Some failure

modes, such as cell flooding, produce characteristic voltage patterns. Unfortunately, most failure modes simply result in a voltage decrease and voltage monitoring alone is insufficient to determine the cause.

3.2.2 Pressure Drop

The pressure drop required to force fuel and oxidant through the cell can shed light on interior processes. Rapid swings in pressure drop are indicative of the blocking and purging of the flow-field with liquid water under flooding conditions. Additionally, a quick decline in pressure drop could indicate a leak – and could possibly be used to cut off reactants before catastrophic failure occurs. However, pressure drop alone cannot indicate other failure modes such as cell dehydration, catalyst poisoning, oxide layer formation etc.

3.2.3 Electrochemical Impedance Spectroscopy (EIS)

The cell's impedance (similar to resistance) to a small AC current is measured over a range of AC frequencies. Different failure modes can be identified by changes in impedance at specific frequencies. This technique does not require the cell to alter its duty cycle but requires expensive equipment to implement. EIS will be discussed in detail in the next chapter.

Chapter 4: EIS as a Diagnostic Tool

EIS is a technique especially well suited to characterize fuel cell performance. It involves the application of a known current or voltage stimulus and measurement of the associated response. The cell's electrochemical impedance, Z, can then be calculated based on the measured system response. The objective of an EIS experiment is to interpret impedance in terms of system properties as functions of controlled variables such as temperature, pressure, etc.

4.1 EIS in the frequency domain

In this study, a small periodic current of known frequency, ω , is superimposed on a steady or slowly varying DC load as shown in figure 4.1 below.

 $I(t) = I_{dc} + I_{ac}sin(\omega t)$



Figure 4.1: Cell Load Components

Normalizing for cell area, A, the current density, j(t) is found by

$$j(t) = j_{dc} + j_{ac}\sin(\omega t) = \frac{I_{dc}}{A} + \frac{I_{ac}\sin(\omega t)}{A}$$
(4.2)

The resulting load, I(t), is drawn from the fuel cell and the voltage response, E(t), is measured directly:

$$E(t) = E_{dc} + E_{ac} \sin(\omega t + \theta) + E(2 \omega t) + E(3 \omega t) + E(4 \omega t) \dots$$

$$(4.3)$$

EIS measurements are only valid for situations where the system response is approximately linear. A linear system is one where the response to the sum of two separate stimuli is the same as the sum of the responses to each stimulus applied separately. For this system to be considered approximately linear, the harmonics in equation 4.3 must be zero or negligible.

(4.1)

The differential equations that govern system response become essentially linear provided that the amplitude of the equivalent voltage perturbation is smaller than the thermal voltage E_T .

$$E_T = \frac{RT}{F} = 25 \text{ mV at } 298 \text{K}$$
 (4.4)

As such, it is important that the current drawn not impose perturbations whose root mean square (rms) is larger than 5mV. This can be verified by examining the local slope of the polarization curve and will be explained in section 5.1.3.

4.2 Complex Impedance

It is possible to represent the AC components of equations 4.2 and 4.3 as complex numbers at frequency ω . They can then be represented graphically in the Argand plane (see figure 4.2)

$$\widetilde{E} = E_{ac} e^{(0)} = E' + iE'', E'' = 0$$

$$\widetilde{j} = j_{ac} e^{(0)} = j' + ij''$$
(4.5)

where $i = \sqrt{-1}$, and θ represents the phase angle between current density and potential. The phase of the potential in figure 4.2 has been arbitrarily set to zero.



Figure 4.2: The Argand Plane

The impedance of the system can now be defined as the ratio between the measured potential and the current stimulus.

$$Z = \frac{\widetilde{E}}{\widetilde{j}} = \frac{E' + iE''}{j' + ij''} = Z' + iZ''$$
(4.6)

where Z' and Z'' represent the real and imaginary components of Z. Note that applying a current and measuring the voltage response is the same as applying a voltage and measuring the current. This equivalence would be lost if the electrical response of the system were non-linear.

4.3 EIS Spectra

As the applied frequency changes, so do the real and imaginary components of impedance. Measuring a fuel cell's impedance at a range of frequencies will produce a continuous curve on the Argand plane. Shown in figure 4.3, this is called a Nyquist plot and is a common way of displaying impedance data.



Figure 4.3: Nyquist Plot

Impedance information is read off the plot in the following manner. At a given point on the curve, the distance to the origin is the magnitude of the impedance and the angle formed with the real axis is the phase angle (see figure 4.3). The main disadvantage of this type of graph is that frequency information is not explicitly displayed.

Bode plots are used to show both the magnitude and phase angle against frequency (see figure 4.4). These charts are better suited to displaying changes in cell impedance and will be the dominant way of displaying data gathered in this study.



Figure 4.4: Measured Bode plots of impedance magnitude (left) and phase angle (right)

4.4 Electrochemical Theory

Impedance represents a measure of the cell's ability to resist the flow of electrical current. It is made up of the sum of three effects: resistive, capacitive, and inductive. Electrochemists try to model fuel cells as AC circuits with capacitors, resistors, and other circuit elements that model fuel cell behaviour. This section will explain what each of the circuit elements represents and how they affect cell impedance.

4.4.1 Resistance

Resistance is a measure of a circuit element's ability to resist the flow of electric current. An ideal resistor has only real impedance and does not change the phase angle of current passing through it. Membrane resistance to ionic transport is often modeled as resistance.

4.4.2 Capacitance

Capacitance is a measure of the ability of two conductors to store electric charge. The impedance of a capacitor is purely imaginary and causes the phase of the current to shift -90° relative to the voltage. The double layer that forms on fuel cell electrodes shows capacitive behaviour.

4.4.3 Inductance

Inductance can be defined as the property of an electric circuit that causes it to store energy in the form of a magnetic field. The impedance of an inductor is purely imaginary and causes current to be phase-shifted $+90^{\circ}$ relative to the voltage. Fuel cells do not have any inductive mechanisms but wires used for fuel cell measurements can have inductive properties. Any positive phase shift seen in EIS measurements is due to so-called *lead inductance* and is a source of error to be minimized.

4.4.4 Warburg and Constant Phase Elements

A full description of the properties of these elements is beyond the scope of this work. However, Warburg and Constant Phase Elements (CPEs) have been introduced to explain electrochemical signatures that do not display purely resistive, capacitive, or inductive behaviour.

The Warburg element can be used to describe impedances associated with mass transport via diffusion ⁽³³⁾. In the case of PEMFCs it models reactant diffusion through the gas diffusion layer (GDL). The CPE is widely used to explain the behaviour of solid ionic conductors, solid-solid interfaces, and rough solid-liquid interfaces ⁽³⁴⁾. A physical interpretation of CPEs is as a measure of electrode surface roughness.

4.4.5 Ambiguous Equivalent Circuits

One of the disadvantages of EIS is that there is not always a single equivalent circuit model to describe a given spectrum. For example, the circuits shown in figure 4.5 all have the same impedance response at all frequencies.



Figure 4.5: Electrical Circuits that generate the same EIS spectra

This study is not concerned with modeling fuel cell behaviour by equivalent circuits but with observable changes in EIS spectra. It is possible that damage caused by thermal cycling could change cell performance in such a manner that its equivalent circuit changes into a second form with exactly the same EIS response. However, the probability of this occurring is exceedingly small.

4.5 PEMFC diagnosis via EIS

EIS has been used to examine SOFCs, MCFCs, PAFCs, DMFCs, as well as PEMFCs ⁽³⁹⁻⁴⁶⁾. Unlike work on thermal cycling, hundreds of studies involving EIS use on fuel cells are available. However, much of the existing research centred on small-scale electrodes, often using half-cells. This thesis focuses on failure modes in operational fuel cells; as such, only the most relevant prior work is discussed below and summarized in table 4.1.

One of the major contributions made by Ciureanu and Roberge was the justification of using a two-electrode measurement technique $^{(7)}$. This setup, in which the anode functions as both the reference and auxiliary electrode has been adopted for subsequent work by Mérida et al. and is used in this study. Ciureanu et al. also used EIS to examine the effects of CO poisoning on Pt and Pt/Ru catalysts $^{(7,45,46)}$.

Work done by Mérida et al. at the University of Victoria serves as a model for this study ⁽¹²⁾. Mérida used EIS to examine cell flooding and dehydration and identified characteristic frequency ranges specific to each failure mode. This was an important step towards developing EIS as a diagnostic tool capable of discerning the cause of cell performance degradation.

This work differs from previous work in the way that EIS is applied (see section 5.1) but its hypothesis that thermal cycling degradation would have impedance effects at specific frequency
ranges is similar. New hardware had to be developed to test this hypothesis experimentally and is detailed in the next chapter.

	Ciureanu et al.	Merida et al.	Connell	
	H Power Enterprises	University of Victoria	(this work)	
Configuration	single cell	4 cell stack	single cell	
Purpose of EIS based Research	Examination of	Differentiation of Flooding	Examination of Thermal	
	Catalyst CO poisoning	and Dehydration Spectra	Cycing Degradation	
Membrane	Nafion 113.5	Nafion 115 Nafion 1		
Active Area/cm ²	25	30.8	25	
Fuel, (Inlet pressure /atm)	H ₂ , (1)	H ₂ , (3)	H ₂ , (2.5)	
Oxidant, (inlet pressure atm)	Air, (1)	Air, (3)	Air, (2.5)	
Humid. Temp/ ^o C (anode){cathode}	(30-60){30-60}	(70-90){70-90}	(72){72}	
Cell Temperature (°C)	25	60-80	75	
Experimental Setup	FRA (Solartron 1250)	FRA (Solartron 1255)	FRA (Solartron 1260)	
	PAR 273A	Voltage Follower	AC load bank	
		DC load bank	DC load bank	
Measurement Configuration	Potentiostatic	Galvanostatic	Galvanostatic	
	2 Electrodes	2 Channels	2 Channels	
	4 Probes	Floating Differential	Floating Differential	
Applied Perturbation (mV AC) {mA AC)	-15	-20	{284}	
Frequency Range /Hz	0.015-10 ³	0.1-4x10 ⁵ 1-10 ⁶		

 Table 4.1: Previous PEMFC Impedance Work

Chapter 5: Experimental Hardware

Before undertaking this study, much of the required hardware had to be designed and built. This hardware can be broken into four general categories:

- Functional modules required to implement EIS
- Cell components
- Temperature control hardware
- Reactant conditioning and stack integrity

For the terminology used in this chapter, *cell* refers to the single PEMFC comprised of an MEA between two bipolar plates. *Stack* refers to both the cell and the support hardware required for reactant delivery, sealing pressure, and current collection as shown in figure 5.1.

With reference to the numerals in figure 5.1, the stack consisted of two graphite bipolar plates (1) separated by an MEA (2). Copper plates (3) were used to collect the electronic current from the stack anode, deliver it to the load bank, and complete the circuit at the stack cathode. Thermoelectric cooler (TEC) arrays (4) were used to control the cell temperature by either delivering heat into or out of the water jacket (5). Ultem plates (6) were used to provide electrical insulation and a pneumatic bladder (7) was used to control the stack sealing pressure. With the exception of the MEAs, all of the stack components were manufactured following the specifications included in Appendix B.



Figure 5.1: Exploded stack schematic (left) and photograph (right)

The following sections describe each stack component, as well as additional hardware, in the context of how they fit into the four categories mentioned above. Figure 5.2 shows a general overview of interrelationships between various components.



Figure 5.2: Hardware Overview

5.1 Functional Modules for the Application of EIS

One major way that this study differs from previous work is in the application of EIS. Previous studies have used a single load bank to apply both the DC and AC components of the load (see figure 5.3).



Figure 5.3: Experimental setup for impedance measurements using a single load bank

This works well in a laboratory setting but most real loads are not able to accept the control signal necessary to generate an AC load. With that in mind, steps were taken to bridge the gap between the laboratory and real applications. A small AC load bank was built to accept the control signal and draw the periodic load from the cell. This load bank is connected in parallel to the main load as shown in figure 5.4.



Figure 5.4: Experimental equipment for impedance measurements using separate load banks

Also shown in figure 5.4 are the functional modules required to measure cell impedance under real operating conditions. The frequency response analyzer (FRA) controls the AC load bank to draw a periodic current from the cell, I_{ac} . However, because the load bank cannot generate current, only draw it, the control signal from the FRA had to be offset:

$$I_{ac} = I_{offset} + I_{periodic} \sin(\omega t)$$
(5.1)

Since this load is parallel to that drawn from the DC load bank, the total current drawn from the cell becomes

$$I_{total} = I_{dc} + I_{ac} = I_{dc} + I_{offset} + I_{periodic} \sin(\omega t)$$
(5.2)

Thus, cell loading is the superposition of two DC loads and one AC load. Visual representations of both I_{ac} and I_{total} are shown in figure 5.5.



Figure 5.5: Components of I_{ac} (left) and I_{total} (right)

The steady state components, I_{dc} and I_{offset} , sum to the mean load drawn from the cell. By varying these components it was possible to examine different areas of the polarization curve. The superimposed AC load generated voltage changes across the stack (V_{stack}) and across a shunt

resistor (V_{shunt}). The responses across the stack and shunt resistor (R_{Ω}) were measured concurrently, allowing the impedance to be calculated as:

$$Z = \frac{V_{stack} R_{\Omega}}{V_{shunt}}$$
(5.3)

5.1.1 Frequency Response Analyzer

The FRA used for this study was an FRA1260 from Solartron Analytical. The machine has two purposes in EIS measurements. First, it generates the control signal for the AC load. The control signal is a voltage that has two components: a steady state component, V_{offset} , and a periodic component, $V_{periodic}$.

$$V_{FRA} = V_{offset} + V_{periodic} \sin(\omega t)$$
(5.4)

These two signal components are directly proportional to I_{offset} and $I_{periodic}$ drawn by the load bank.

Secondly, the machine measures the voltage changes across the stack and shunt that are used to calculate impedance by equation 5.3. The FRA was connected to a computer using an IEEE488 interface board and controlled using two commercial software packages, Zplot and Zview ⁽³⁵⁾, to perform online analysis.

5.1.2 DC Load Bank

An electronic TDI-SDL1047 load bank was used to sink I_{dc} , the majority of the current (94-98.5%) drawn from the cell. The load bank was integrated into a Greenlight FCAT800-S test stand, which provided computerized control of the load. The desired load was simply input to the software and was maintained by internal control loops.

5.1.3 AC load bank

Since the required equipment was not commercially available, a custom AC load bank (shown in figure 5.6) was designed and built. The advantages of this load bank were two-fold; not only was it designed to interface with the equipment used in this study but it also allowed EIS to be performed at frequencies as high as 1 MHz while most commercially available load banks are rated for hundreds of kilohertz. The circuit diagram for the load bank is included in Appendix C. This piece of hardware is central to the goal of moving EIS from the laboratory into practical diagnostic applications.

As discussed in Section 4.1, EIS requires that a small periodic load be superimposed on steady or slowly varying DC load. Since most real loads cannot accept the control signal needed to

generate a periodic load, the technique was restricted to the laboratory. By using the AC load bank to generate the periodic load, EIS can be run on a fuel cell powering any steady load when the two loads are connected in parallel.



Figure 5.6: AC Load Bank

The flow of current drawn by the AC load bank was controlled by a signal, V_{FRA} , from the generator channel in the FRA. A control signal of 1V corresponded to a current of 0.5A drawn by the load bank. The magnitude of V_{FRA} used for experimentation was

$$V_{FRA} = 0.6V + 0.4V_{RMS}\sin(\omega t) \tag{5.5}$$

This corresponds to a current drawn by the load bank of 0.3 ± 0.283 A. The periodic current drawn by the load bank is 200mA_{RMS}, or 8mA_{RMS}/cm². As discussed in section 4.1, it is important that this not cause a voltage change greater than 5mV_{RMS} to preserve linearity. The slope of the polarization curve gives the relationship between the voltage and current density. Therefore, it is important that these measurements be taken only on portions of the polarization curve that have a slope with an absolute value below $0.625 \Omega \text{cm}^2$.

5.2 The Cell

The functional unit of a PEMFC stack is a single cell consisting of an MEA surrounded by two bipolar plates. This work in this study was done on a single cell as described below.

5.2.1 Bipolar Plates

The bipolar plates were made of graphite and had a flow-field pattern milled into one side. The pattern was a simple serpentine path covering the active area of the cell (see figure 5.7 and appendix B for full engineering drawings).



Figure 5.7: Anode plate, cathode plate and photograph

The width of the channel, and hence number of passes was different for the anode and cathode plates to compensate for the different viscosities and equalize the pressure drop on each side of the MEA. Measured pressure drop values are shown in figure 5.8.



Figure 5.8: Measured anode and cathode pressure drop

All plates in the stack contained holes in the corners to accommodate longitudinal alignment rods. The rods were made from non-conductive Delrin plastic to prevent short-circuiting the cell. A hole was drilled in the centre of the cathode plate so that a thermocouple could be placed directly into the gas stream. The thermocouple was sealed into place using a two-part epoxy. A small channel was drilled into the back of the bipolar plate to accommodate the thermocouple lead wire.

To seal the bipolar plates against the MEA, a channel was drilled around the active area to seat a silicone gasket. Silicone seals were also used to ensure integrity at the gas inlets and outlets. They are discussed in more detail in section 5.4.3

The plates also had grooves cut into the sides (see figure 5.9). These allowed the plates to be clamped together using binder clips once the MEA and internal gaskets had been aligned. This

eliminated the problem of the MEA shifting before stack sealing pressure could be applied. The binder clips were then removed after sealing to prevent short-circuiting the stack.



Figure 5.9: Binder clips used to keep the MEA from shifting in the cell during insertion into the stack

5.2.2 Membrane Electrode Assemblies

The MEAs used for this study were provided by E-Tek. The membranes were made of Nafion 115 with an active area of 25cm^2 and a Toray carbon paper GDL. MEA specifications are given in table 5.1. The polymer area exceeded the active area and matched the bipolar plate dimensions. The extra membrane material was used as a sealing surface for the internal gaskets and was trimmed into an octagonal shape to avoid the alignment rods (see figure 5.10).

ETEK A-9 MEA/PEMFC/060					
Membrane	Nafion 115 - Size: 10cm x 10cm				
GDL type	Toray Carbon paper TGPH-060				
Active Area	tive Area SS/ELAT/060 - Size: 5cm x 5cm				
Catalyst type	20% Platinum on Vulcan XC-72				
Catalyst loading	0.5 mg/cm^2				

 Table 5.1: MEA specifications



Figure 5.10: Trimmed MEA

While not high performance, the E-TEK membranes were chosen for their repeatable performance ⁽³⁶⁾.

5.2.3 Voltage Probes

Female copper receptors were press-fit into holes drilled directly into the graphite plates (figure 5.11). Male pins that snap into the receptors were then attached to voltage probes allowing both

DC potentials and cell impedance measurements to be made directly from the graphite plates. This method allowed for quick attachment and removal of the voltage probes during stack assembly and disassembly.



Figure 5.11: Voltage probes

5.3 Thermal Control Hardware

Stack temperature was controlled using a combination of thermoelectric coolers (TECs) and a closed hot water loop. The hot water loop flowed through manifold plates, acting as water jackets, built into the stack (see figure 5.1). When steady temperatures were required, the water jackets were used alone to control stack temperature due to their accuracy and stability. During thermal cycling, the TECs and water jackets were used in tandem to rapidly change cell temperature.

5.3.1 Manifold Plates

The manifold plates had a dual role in the stack. They acted both as a water jacket to control stack temperature and housed the fittings for reactant and product delivery to and from the cell. Both of the water jackets in the stack are composed of two plates. Shown in figure 5.12, the outer manifold plates were made from half-inch 316L stainless steel. Inlet and outlet ports were drilled into the side for both cooling water and reactants (see appendix B for full engineering drawings). The temperature of the water in the channel between the manifold plates was controlled such that cell temperature (measured by the thermocouple placed directly into the bipolar plates) reached the desired set point.



Figure 5.12: Stainless steel manifold (left) gold-plated copper end plate (middle) and photograph (right)

A groove was milled around the water channel to seat a silicone gasket for sealing. A piece of gold-plated copper (figure 5.12) was used as the inner component of the water jacket (figure 5.13). Copper was chosen for its favourable heat transfer properties and was gold coated to avoid corrosion. Using copper, with a thermal conductivity of 400 W/mK against the cell and stainless steel, with a thermal conductivity of 14 W/mK ⁽³⁷⁾ as the outer plate helped to ensure that the majority of the heat from the water jacket went into the cell, and not into other stack components. The tab on the copper plate stemmed from its use as a current collector in experiments external to this study.



Figure 5.13: Water Jacket - conceptual drawing (left) and photograph (right)

The other role of the manifold plates is reactant delivery. Ports on the stainless steel section allow inlet and outlet streams to connect to the test stand (section 5.4.1) that provided conditioned reactants. From the manifold, reactants were passed through the TEC array and into the cell. Silicone gaskets (see section 5.4.3) were used internally to provide seal integrity.

5.3.2 Cooling Cart

The temperature of the water in the cooling jackets was controlled using a G6610-CC-001-2003 cooling cart provided by Greenlight (see figure 5.14). The cart controlled the temperature of a

closed loop of DI water using electric heaters and a heat exchanger chilled by domestic cold water. Integrated Omega temperature controllers were used to set the desired water temperature. Alternatively, the temperature could be controlled directly from the Greenlight test stand (section 5.4.1)



Figure 5.14: Cooling Cart

The high thermal mass of the water in the cooling cart allowed stack temperature to be maintained within 0.1 degree Celsius of the set point. The disadvantage of high thermal mass is the length of time required to change temperature within the cell. This necessitated the dual system using TECs, described below, for thermal cycling.

5.3.3 Thermoelectric Cooler Array

TECs are solid-state heat pumps used in applications where temperature stabilization, thermal cycling, or cooling below ambient are required. They work based on the Peltier effect by which DC current applied across two dissimilar materials causes a temperature differential.

The typical thermoelectric module consists of two thin ceramic wafers with a series of P and N doped semiconductors sandwiched between them. The ceramic material on both sides of the thermoelectric adds rigidity and the necessary electrical insulation. The N type semiconductor has an excess of electrons, while the P type has a deficit of electrons. One P and one N make up a couple, as shown in Figure 5.15. The TECs used for this study each contain 71 such couples.



Figure 5.15: TEC Components

As the electrons move from the P type material to the N type material through an electrical connector, the electrons jump to a higher energy state absorbing thermal energy (cool side). Continuing through the lattice of material, the electrons flow from the N type material to the P type material through an electrical connector, dropping to a lower energy state and releasing energy as heat to the heat sink (hot side).

Changing the direction of the DC current has the effect of switching the hot and cold sides of the TEC. This property allows the TECs to both heat and cool the stack depending on the polarity of the applied current. Shown in figure 5.16, the coolers used in this study were HT8-7-30 models provided by Melcor Inc. The TECs were arranged on the current collector as shown in figure 5.17. A thin layer of grease was used to both hold the TECs in place and improve heat transfer with the collector. Delrin spacers were epoxied to the corners of the array to locate the gaskets that pass reactants from the manifold to the cell.



Figure 5.16: Melcor HT8-7-30 (left) and TEC Array conceptual drawing (right)

TECs are heat pumps that use electrical work to transfer heat from cold areas to warm ones. The amount of heat transferred by TECs depends on the applied voltage and the temperature difference between the plates. Heat transfer curves for HT8-7-30's are shown in figure 5.17.



Figure 5.17: Lines show voltage required and heat transfer at constant current for a single TEC (Courtesy of Melcor Inc.)

These curves were used as a basis for heat transfer calculations included in appendix D. As shown, TECs become less efficient at cooling as the temperature difference between the plates grows. This is because the larger currents needed to increase the cooling load lead to increased ohmic heating within resistive elements of the TECs. The opposite was true when TECs are used to heat the cell; the ohmic heating within the TECs works in tandem with the Peltier effect to rapidly increase cell temperature.

The TEC array was placed between the cell and the water jacket. When current was applied such that the cell-side of the TECs was the hot side, heat was taken from the water jacket to increase cell temperature. When the direction of the current was switched, the cell-side became the cool side and heat was dumped to the water jacket.

In this manner the water jacket acted as both a heat source for cell heating and a heat sink for cell cooling. To ensure that the temperature difference between the plates remained as small as possible, the water jacket was run at an intermediate temperature between the desired high and low temperatures of the thermal cycle. Since TECs can heat more efficiently than they cool, keeping the water temperature closer to the desired cycle low minimized cycle times. For experiments that cycled between 20-80°C, the water jacket was maintained at 35°C. Under these conditions, the cell temperature was cycled from 20°C up to 80°C, held at 80°C for 10 seconds then returned to 20°C and held there for 10 seconds; all in under three minutes.

It was found that when the temperature gradient was most favourable (heating from 20° C or cooling from 80° C) the cell temperature would change as fast as 2° C per second (see figure 5.18). This rapid temperature change ran the risk of introducing failure modes that would not be seen under normal cell heating and cooling. As detailed in the next section, measures were taken to keep cell temperature change below 1° C per second.



Figure 5.18: Measured rate of stack temperature change as a function of stack temperature

5.3.4 TEC Control Apparatus

The goal here was to design a method of switching the direction of the current to the TECs automatically. The equipment used to accomplish this goal included: a Mean Well PSP-1000-15 900W DC power supply, a National Instruments DAQ system with a (board name) variable DC output, and a custom built switching mechanism. The power supply delivered current at 12.6-18VDC. Therefore, examining the TEC power consumption curves in figure 5.17, the TECs were connected as shown in figure 5.19 giving the option of 6.3-9V per cooler.



Figure 5.19: TEC Array Electrical Connections

The switching mechanism used two-pole relays to mechanically change the direction of the current. A simple circuit board (see figure 5.20) was designed and built to allow the relays to accept a 5V control signal from the DAQ system. LabviewTM software was used to generate an appropriate control signal.



Figure 5.20: a) Relay schematic b) switching mechanism circuit diagram c) photograph

The relays alternated between two positions based on the charge of an electromagnetic coil. When uncharged, a spring maintained connection with the contacts at the bottom of 5.20a. When the coil was charged, the linkage was magnetically attracted and connected to the contacts near the coil. Referring to figure 5.20a, when unpowered, the current through the TECs will be in the same direction as the current to the relay. When the coil is charged, current through the TECs will flow in the opposite direction.

The output signal from the DAQ system did not have enough power to charge the coil. Therefore, the relays were connected in parallel to the TECs and powered by the same power supply. Metal-Oxide Semiconductor Field Effect Transistors (MOSFETs) were used to control the flow of current into the coil. MOSFETs are circuit elements that can be conductive or non-conductive based on the presence or absence of a 5V control signal (see figure 5.20b). In this case, the DAQ output was sufficient to control the MOSFETs. Diodes and resistors were added to the circuit board to protect equipment against ground loops or improper electrical connections.

As mentioned in the previous section, simply allowing the TECs to heat or cool continuously resulted in unacceptably high temperature changes within the cell. To counter this problem, LabviewTM was programmed to provide a series of heating and cooling commands in rapid succession providing a damped heating or cooling curve and keeping temperature changes below 1°C per second.

5.4 Support Equipment

This section discusses equipment necessary to support fuel cell operation. Such functions include reactant conditioning and delivery, and seal integrity.

5.4.1 Reactant Conditioning and Delivery

A fuel cell stack cannot work in isolation. Conditioned fuel and oxidant streams must be delivered to the stack. To accomplish these tasks, the stack was connected to a Greenlight

FCAT-800S test stand. The operation of the test stand has been extensively documented elsewhere ⁽³⁸⁾. Only a brief description of the main components will be included here.

Reactant streams must be properly humidified and heated prior to entering the fuel cell. This was accomplished by boiling DI water and injecting it into the inlet streams. The inlet streams were then independently cooled to a set temperature in *knockout vessels*. Excess water condensed out of the streams, which were then re-heated before entering the cell. Both the temperature of the saturated stream leaving the knockout vessels, and the temperature entering the cell were user defined and maintained by internal control loops.

The test stand also controlled other functions, such as: reactant pressures, flow rates, and stoichiometries. These are discussed in further detail in section 6.4 as they relate to experimental conditions. An integrated DAQ system recorded all relevant values.

5.4.2 Pneumatic Bladder

The pressure inside a pneumatic bladder controlled stack-sealing pressure. Shown in figure 5.21, the bladder was a circular cavity topped with an o-ring. The bladder cap sealed against the O-ring and was held in place with tie-rods. The bladder cap had two ports, one to accommodate input compressed air and a second for a pressure gauge.



Figure 5.21: Pneumatic Bladder and Bladder Cap

To seal the stack, the bladder cap was positioned and the tie rods moved into place. The wing nuts on the tie rods were then tightened to compress the O-ring. The bladder was then pressurized to a level set by an upstream regulator. The air pressure pushed upwards on the bladder cap, lessening the compression of the O-ring. This necessitated a re-tightening of the wing nuts to prevent leaks past the O-ring.

The tie rods used to hold the bladder cap in place were attached to the stack base by pins, allowing them to rotate (see figure 5.22). This feature was added to ease the MEA replacement process. Having the tie rods lie flat makes the process of removing the cell from the stack more convenient.



Figure 5.22: The tie rods used for stack compression swing flat when not in use

5.4.3 Silicone Gaskets

Much of the sealing between stack components was done with custom made silicone gaskets. These gaskets were used to seal the MEA between the bipolar plates, the water jacket inside the manifold plates and to move reactants from the manifold to the cell and back (see figure 5.23).



Figure 5.23: From left to right - the MEA, water jacket, and reactant gaskets

The gaskets were made by casting a mixture of J-RTV silicone and catalyst. The MEA and water jacket gaskets were set in moulds made from Delrin while the reactant gasket moulds were made of aluminum. Engineering drawings of the moulds can be found in appendix B.

The silicone mixture was degassed in a vacuum below 5kPa for 15 minutes prior to casting. The cast silicone was then cured at 80°C for one hour. Post processing was required for the reactant gaskets and involved drilling a hole through the centre of each. This was accomplished by drilling the gaskets while they were still in their aluminum mould. Expansion of the gaskets during the setting process provided enough frictional force to keep the gaskets from slipping in the mould during drilling.

Chapter 6: Experimental Method

The focus of this thesis was the generation of hardware required to allow the diagnosis of thermal cycling by EIS. Ensuring that the equipment works was central to that goal. As such, experimentation was carried out both to demonstrate that equipment performance is acceptable and to serve as a roadmap for further testing. This chapter details the experimental method used for verification. The level of detail is such that this chapter can serve as a guide for anyone looking to continue this investigation or perform a similar analysis.

6.1 Presentation of Polarization Curves

Many reports present polarization curves as a single line. This is simply not the case. Variation in factors such as cell temperature, reactant pressure, and cell hydration can have significant effects on instantaneous cell performance. The DAQ system integrated into the test stand took continuous measurements, including during transitional states, providing the polarization data in figure 6.1a.



Figure 6.1: a) all polarization data, b) stabilized data curve, c) averaged stabilized values

Eliminating transitional data, the curve becomes clearer, as shown in figure 6.1b. These points come from measurements taken after the voltage had stabilized at each current density. Stabilization time varied from measurement to measurement but was generally in the range of 2-5 minutes.

In order to make the data more legible for simplified comparison, polarization curves from this study are presented using averaged values of data obtained after voltage stabilization (figure 6.1c). Unless otherwise stated, variation in measurements taken after stabilization was less than 5mV. Stabilized values are averaged over 4-10 measurements taken over time periods ranging from 30 seconds to 5 minutes.

6.2 MEA Conditioning

New MEAs must be fully hydrated before optimal performance occurs. To accomplish this, the MEAs were run at moderate loads for several hours prior to testing. Over time, the performance increased and then leveled off as the MEA became fully conditioned. Figure 6.2 shows the contrast between polarization curves for a new MEA and a fully conditioned MEA.



Figure 6.2: Measured Effects of MEA Conditioning

The goal was to bring each MEA to the same starting point before testing began, helping to ensure repeatability in the measurements. Unfortunately, this took a different amount of time for each MEA, which made conditioning over a set time period impractical. As an alternative, each MEA was conditioned until performance increases had stopped or slowed to a level of less than 1mV per hour for two consecutive hours. It was found that performance at low to moderate current densities ($j < 0.6A/cm^2$) stabilized faster than at higher current densities. It was also found that leaving the cell under constant load was insufficient to fully condition the cell.

The cells were conditioned in *galvanostatic* or current-following mode. When left under constant load, performance improvements, in the form of increased voltage, would quickly level off. However, by switching between 2 or 3 loads, the leveling would occur at progressively higher voltages. It was also found that the mass transport limit increased more rapidly if it was "pushed" by conditioning at high current densities. This was accomplished by periodically increasing the load until the potential dropped to 0.2V. An example of a typical cell conditioning run is included in appendix E. The MEAs were conditioned at the same temperature, pressure, and humidity as was used during experimentation.

6.3 Experimental Procedure Overview

After the MEA had been fully conditioned, a preliminary polarization curve and EIS spectra were obtained to establish initial performance. EIS spectra were taken at four different current densities. The loads chosen were 0.2, 0.4, 0.6, and $0.8A/cm^2$ respectively (see figure 6.3a) and the data is presented in both Nyquist and Bode plots for each run (figures 6.3b and 6.3c). These loads were selected to cover a wide range of the polarization curve without encroaching into areas that would prevent linearity of the measurement (see section 5.1.3 for details). Practically, this means that impedance measurements were made mostly in the ohmic region. Polarization curves were plotted covering the range of $0 - 1.04A/cm^2$.



Once the initial data had been gathered, the load was disconnected and the test stand shut down in preparation for thermal cycling. During cycling, no reactants were passed through the cell and no load was drawn. The cooling cart temperature was lowered to 35° C and the TECs were used to drop cell temperature to 20° C. Labview was then used to control the TECs cycling the cell between 20 and 80° C 99 times using the procedure outlined in section 5.3.3.

After 99 cycles, the TECs were disengaged, the cooling cart temperature was raised to bring cell temperature to a steady 75°C and load was once again drawn from the cell. It was found that cell dehydration occurred during cycling. Therefore, the MEAs were reconditioned for one to 1.5 hours before further data was gathered.

After reconditioning, a polarization curve and EIS spectra were taken to establish cell performance after 100 thermal cycles using the same procedure listed above. In early experiments polarization curves and EIS spectra were obtained after 10 and 50 cycles as well but it was found that the performance difference was negligible. Therefore, 100 cycles was chosen as the first relevant measurement.

The entire process was repeated and measurements taken after 250, 500, 1000, and in one case 2000 cycles. The next section provides a detailed explanation of how relevant variables were controlled during experimentation.

6.4 Control Variables

A list of the variables that can be controlled with this apparatus include: stack sealing pressure, reactant pressure, reactant humidification, reactant flow rates, stoichiometry, stack operating temperature, maximum and minimum cycle temperature, number of cycles, and load.

This presents an overwhelming number of options when it comes to possible experiments. This section describes which variables were held constant, how the values were maintained and the accuracy.

6.4.1 Reactant Pressure

Anode and cathode reactant streams were pressurized to 150 kPa for all experiments presented in this work. Elevated pressures were used to increase performance and allow measurements to be made at higher current densities. It was found that cell flooding became an issue when pressures were increased beyond 150 kPa. The Greenlight test stand was able to maintain pressures to within ± 0.5 kPa of the setpoint.

6.4.2 Load

As mentioned in section 6.3, EIS spectra were taken at 4 different current densities and polarization curves plotted covering the range of 0 - 1.04 A/cm². For each measurement, the desired load was simply entered into the test stand software and was automatically maintained by internal control loops. The measured value of the load never strayed from the set point. Therefore the accuracy of the measurement was within ±0.01A, the resolution of the measurement.

6.4.3 Reactant Flow Rates

One of the most convenient features of the Greenlight test stand is an option called *load* following mode. In this mode the reactant flow rates are calculated and automatically adjusted based on the desired load and stoichiometry. Mass flow controllers maintained the reactant flows within $\pm 2\%$ of desired rates.

6.4.4 Stoichiometry

The stoichiometries chosen were 4 and 6 for the anode and cathode respectively. The reason for this decision was two-fold. Primarily, this was done because the cell was somewhat undersized for the test stand. At these stoichs, the minimum flow rates that the test stand could control accurately corresponded to a current density of 0.15A/cm². If the stoichiometries were halved, the minimum controllable flow would correspond to 0.3A/cm², which was considered unacceptably high. For polarization curve measurements taken at current densities below

0.15 A/cm², load following was turned off and the reactant flows corresponding to 0.15 A/cm² were used.

6.4.5 Stack Operating Temperature

When stack loading was changed the stack temperature also changed slightly due to changes in heat flux with the inlet and outlet gas streams and heat generated within the stack. When the load was changed, stack temperature was maintained by adjusting the temperature of the water from the cooling cart.



Figure 6.4: Impedance variation with temperature

As shown in figure 6.4, stack temperature had a significant effect on EIS spectra. The highest impedance occurred at 50°C, it then decreased until the minimum recorded value at 73.5°C and increased again as temperatures continued to rise. This shows that impedance was minimized somewhere between 73.5°C and 78.5°C and is the reason that stack temperature was maintained at 75°C for all of the experiments presented in this study. To minimize the effects of temperature variations, measurements were only taken once stack temperature had settled to 75±0.2°C.

6.4.6 Maximum and Minimum Cycle Temperature

Two temperature ranges were chosen for this study. The first range examined was 20-80°C; this was the desired range for thermal cycling. Eighty degrees was chosen as an upper limit since it is representative of fuel cell operating temperatures. Twenty degrees was chosen both as representative of ambient environmental temperatures and as a safe temperature for TEC operation. Since the TECs are capable of cooling below ambient temperatures, it is possible to have a cycle minimum below room temperature with this apparatus. However, care must be taken not to drop temperatures below the local dew point or liquid water can condense out of the air and short-circuit the coolers.

The TECs were consistent in their ability to hold the maximum and minimum cycle temperatures over hundreds of cycles. Minimum and maximum temperatures were reached within $\pm 0.5^{\circ}$ C except for the first few cycles when the system was stabilizing and variability was $\pm 2^{\circ}$ C

Preliminary experiments (included in appendix F) were carried out before the TECs were in place to test the EIS equipment. These experiments used the cooling cart alone to cycle cell temperature, presenting two disadvantages. First, the cycle time was much longer, approximately 15 minutes per thermal cycle. Second, since the cooling cart could not cool below ambient temperatures, cooling became quite inefficient as room temperature was approached. In fact, using the cooling cart alone, it would take nearly 10 minutes to cool the stack from 30° C to 20° C.

Therefore, during the preliminary tests, the stack was cycled between 30 and 90° C to maintain the same 60° C difference. It was found that the cell received much more damage during this test than later tests cycling between $20-80^{\circ}$ C. However, it was not clear whether the difference was due to the difference in temperature range or to poor experimental procedure that did not give the cell enough time to fully recover between tests. Therefore, this temperature range was repeated using the TECs and the procedure mentioned in section 6.3.

6.4.7 Stack Sealing Pressure

Stack sealing pressure was read off an analog gauge. The gradation on the gauge was 2PSI. Therefore the accuracy of the pressure measurement is ± 1 PSI.

6.5 Impedance Measurements

Impedance spectra were taken for the frequency range from 1MHz to 1Hz. In order to minimize the error in each measurement, the FRA was programmed to use the average of many readings taken at a particular point. To minimize the effects of noise, it was important to have at least 25 measurements to average. The FRA could either take averages based on a set number of cycles or average over a set time period. Trying to capture the entire frequency range with either scheme alone proved troublesome.

Higher frequencies encounter more noise from sources such as CRT monitors (400 kHz) and radio waves (typically 150 kHz and up) and required a larger number of samples in the measurement. Averaging over a large number of samples was not a problem at high frequencies; however, taking samples over several hundred cycles at frequencies below 10Hz would lead to long experiments.

Another option was to average samples gathered over a set period of time. That way higher frequencies get more samples without slowing things down at low frequencies. However, the problem again came at frequencies below 10 Hz where averaging over a few seconds would not provide enough samples for a proper measurement.

The solution to this problem was to break the frequency range into two measurements. One from 1 MHz to 10Hz averaged over 2 seconds, and another from 50Hz to 1Hz with 50 cycles per measurement. This ensured that all data were well averaged and provided an overlap range to verify agreement between the two measurements. When there was agreement in the overlap range, the data from the 50Hz-1Hz measurements was used. When there was no agreement, both data sets were re-measured.

Chapter 7: Measurements and Results

This chapter details the EIS measurements obtained to verify that the equipment works. Each section begins with the raw data obtained. Relevant results are then presented and discussed. Appendix G gives details on how to obtain the full data set from this study.

This chapter will focus on data gathered from five experimental runs. The first two runs established baseline performance. They acted as control groups to determine what damage the cell took under experimental conditions without thermal cycling. The final three runs gathered impedance data to assess the effects of thermal cycling. The chapter breaks down as follows:

- 7.1: Baseline run 1, EIS measurements taken from bipolar plates
- 7.2: Baseline run 2, EIS measurements taken from current collectors
- 7.3: Thermal cycling Run 1, 20-80°C, measurements taken from bipolar plates
- 7.4: Thermal cycling Run 2, 20-80°C, measurements taken from current collectors
- 7.5: Thermal cycling Run 3, 30-90°C, measurements taken from bipolar plates

After the data has been presented and analyzed, the following areas pertinent to the results are discussed:

- 7.6: Formation of Contact Resistance
- 7.7: Assessment of Cell Damage
- 7.8: Relevant Frequency Ranges

7.1 Baseline Run 1, EIS Measurements Taken From Bipolar Plates

In order to accurately assess the effects of degradation due to thermal cycling it is necessary to eliminate or account for other sources of performance improvement or degradation. As discussed in section 2.4, many of the sources of cell failure can be prevented or minimized in a laboratory environment. The effects of cell flooding, dehydration, and catalyst poisoning have been eliminated from this experiment leaving only effects of contaminants and performance degradation with time as concurrent factors reducing cell performance. Additionally, even though every effort was made to ensure cell conditioning was complete before testing began, continued cell conditioning can work to increase cell performance over time.

While these effects are expected to be minimal, the only means of verification was to measure their effect on cell performance so that it could be discounted from thermal cycling damage. To accomplish this baseline trials were run without thermal cycling.

The baseline procedure was identical to that listed in section 6.3 except that the cell was left at 20°C instead of being thermally cycled between measurements. The cell was shut down for the same period of time as if it would have been thermally cycled. For example, after the initial data were taken, a regular run would have undergone 99 cycles at three minutes each for a total of 4 hours 57 minutes. The baseline cell was left at 20°C for this time and the experiment was resumed. All other factors were the same.

The conditions for the baseline test are given in table 7.1 and impedance data and polarization curves are shown in figures 7.1-7.3. Note that the number of thermal cycles for this run is listed as 5 since the cell was operated and shut down 5 times (at times equivalent to 1,100,250,500, and 1000 cycles) during testing.

Baseline Run 1 Conditions							
Stack		Anode		Cathode			
Temperature Cycled (°C)	20-75	Pressure (kPa)	150	Pressure (kPa)	150		
Number of Cycles	5	Dew Point (°C)	72	Dew Point (°C)	72		
Stack Sealing Pressure (PSI)	120	Inlet Temp (°C)	80	Inlet Temp (°C)	80		
Cell Operating Temperature (°C)	75	Stoichiometry	4	Stoichiometry	6		

Table 7.1:	Baseline Run	1	- experimental	parameters
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Figure 7.1: Measured polarization curves for Baseline Run 1



Figure 7.2: Measured cell impedance as a function of current density and thermal cycling



Figure 7.3: Measured cell impedance at 0.8A/cm² as a function of thermal cycling

Polarization curves in figure 7.1 show that cell performance remained steady over the test. Final performance was within 1% of initial performance at all current densities.

The results from this baseline test show that impedance and phase angles obtained stayed relatively constant over the time corresponding to 1000 cycles. Measured impedance magnitude and phase angle values are normalized against measured averages in figure 7.4. The graphs shown in figure 7.4 were selected as being representative of the normalized data. Charts showing normalized measurements at all current densities are provided in the full data set, see Appendix G for details.

Variation in the impedance measurements was $\pm 5\%$ over frequencies below 50kHz. Phase angle variation was $\pm 5\%$ between 50kHz and 100Hz and rose to $\pm 10\%$ at frequencies below 100Hz. The increase in variability at lower frequencies is explained by the fact that phase angle values approach zero at low frequencies, so any measurement errors become relatively larger. The erratic impedance behaviour at frequencies above 50 kHz is discussed in detail in section 7.8.



Figure 7.4: Normalized impedance magnitude (top) and phase angle (bottom) values

The notable exception to measurement stability occurred at 0.8 A/cm² over the frequency range 500-10000 Hz for both phase angle and magnitude (figure 7.5). This behaviour is indicative of a non-linear measurement, which would make the impedance measurement invalid. As discussed in section 5.1.3, non-linearity occurs when the local slope of the polarization curve exceeds $|0.625| \Omega \text{cm}^2$. The limit of impedance as frequency approaches zero is the local slope of the polarization curve. According to calculations in appendix D, the local slope at 0.8 A/cm² ranged between 0.58 and 0.61, supporting this theory.



Figure 7.5: Normalized impedance (top) and phase angle (bottom) values at 0.8A/cm²

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7.2 Baseline Run 2, EIS Measurements Taken from Current Collectors

This run was identical to 7.1 except that the impedance measurements were obtained from the copper collectors instead of directly from the graphite plates. Any increase in contact resistance between the bipolar plates and copper collectors that is not caused by thermal cycling will show up here.

Baseline Run 2							
Stack		Anode		Cathode			
Temperature Cycled (°C)	20-75	Pressure (kPa)	150	Pressure (kPa)	150		
Number of Cycles	5	Dewpoint (°C)	72	Dewpoint (°C)	72		
Stack Sealing Pressure (PSI)	30	Inlet Temp (°C)	80	Inlet Temp (°C)	80		
Cell Temperature (°C)	75	Stoichiometry	4	Stoichiometry	6		

 Table 7.2: Experimental Parameters for Baseline Run 2



Figure 7.6: Measured polarization curves for Baseline Run 2



Figure 7.7: Measured impedance data as a function of current density and thermal cycling



Figure 7.8: Measured impedance data at 0.8A/cm² as a function of thermal cycling

Examination of the polarization curves shows that cell performance did not decrease over the test. After 500 equivalent cycles, cell performance was within $\pm 0.5\%$ of initial performance. Measurements taken after 1000 equivalent cycles showed a voltage increase. The increase was moderate at current densities below $1A/cm^2$ where the largest performance increase was 7mV at $0.8A/cm^2$. At higher current densities the potential increase ranged from 3.8-14.3 percent. This suggests that the voltage increase may be due to increased conditioning at the higher current densities (see section 6.2).

Normalized impedance data were generated and representative charts are shown in figure 7.9. All normalized data from this run are available in the full data set, see Appendix G for details. Measured values were stable for all runs except at 1000 cycles where impedance decreased, corresponding to an increase in cell performance. Impedance values were $\pm 3\%$ for all runs and less than $\pm 2\%$ if the 1000 cycle measurements are omitted. Phase angle values were less stable, at $\pm 8\%$ for all runs above 10Hz and $\pm 5\%$ omitting measurements at 1000 cycles. Again, variation increased at low frequencies due to the phase angle measurements approaching zero.



Figure 7.9: Normalized impedance magnitude and phase angle values

7.3: Thermal cycling Run 1: 20-80°C, measurements taken from bipolar plates

In this experiment the cell temperature was cycled between 20 and 80°C and impedance measurements were made directly from the bipolar plates. After 1000 cycles, it was found that cell performance had not decreased significantly. It was therefore decided to continue testing up to 2000 cycles. Again performance decreases were negligible.

Thermal Cycling Run 1						
Stack		Anode		Cathode		
Temperature Cycled (°C)	20-80	Pressure (kPa)	150	Pressure (kPa)	150	
Number of Cycles	2000	Dewpoint (°C)	72	Dewpoint (°C)	72	
Stack Sealing Pressure (PSI)	120	Inlet Temp (°C)	80	Inlet Temp (°C)	80	
Cell Temperature (°C)	75	Stoichiometry	4	Stoichiometry	6	

Table 7.3: Experimental parameters for Thermal Cycling Run 1



Figure 7.10: Measured polarization curves for Thermal Cycling Run 1



Figure 7.11: Measured impedance data as a function of current density and thermal cycling


Figure 7.12: Measured impedance data at 0.8A/cm² as a function of thermal cycling

The performance change over 2000 cycles was less than $\pm 0.5\%$ for current densities below $0.8A/cm^2$. At higher current densities performance increased slightly, possibly due to improved conditioning.

Figures 7.13 and 7.14 show differential $(Z-Z_o)$ and normalized impedance data. To better emphasize impedance changes, the values have been normalized against the initial run (Z/Z_o) . The most significant changes occur at frequencies between 10 and 1000Hz. The increase at frequencies over 50kHz is exaggerated in the normalized plot due to measured impedance values approaching zero at high frequency. Erratic results at frequencies above 50kHz are discussed in section 7.8.



Figure 7.13: Differential between initial and subsequent impedance measurements at 0.2A/cm²



Figure 7.14: Normalized impedance magnitude measurements for 0.2A/cm²

Shown in figures 7.15 and 7.16, the most significant phase angle effects were observed at frequencies between 10 and 100Hz. All differential and normalized charts for this experiment are provided in Appendix G.



Figure 7.15: Differential phase angle values for 0.2A/cm²



Figure 7.16: Normalized phase angle values for 0.2A/cm²

7.4: Thermal Cycling Run 2: 20-80°C, Measurements Taken from Current Collectors

It was hypothesized that stack sealing pressure may have an effect on thermal cycling damage due to thermal expansion of various stack components. To test this theory, an experiment was run with stack sealing pressure tripled.

Thermal Cycling Run 2								
Stack		Anode		Cathode				
Temperature Cycled (°C)	20-80	Pressure (kPa)	150	Pressure (kPa)	150			
Number of Cycles	1000	Dewpoint (°C)	72	Dewpoint (°C)	72			
Stack Sealing Pressure (PSI)	350	Inlet Temp (°C)	80	Inlet Temp (°C)	80			
Cell Temperature (°C)	75	Stoichiometry	4	Stoichiometry	6			

Table 7.4:	Experimental	parameters for	Thermal	Cycling Rur	12
	The second s				



Figure 7.17: Measured polarization curves for Thermal Cycling Run 2



Figure 7.18: Measured cell impedance as a function of current density and thermal cycling



Figure 7.19: Measured impedance data at 0.8A/cm² as a function of thermal cycling

Unlike the baseline runs, this one showed a measurable performance decrease. The difference between peak performance, at 10 cycles, and final performance reached as high as 0.057 mV/cycle at 0.8A/cm^2 . A chart of average voltage decrease as a function of current density is shown in figure 7.20.



Figure 7.20: Average potential loss per cycle over 990 cycles

Similarly, as shown in figure 7.21, there were significant changes to the EIS spectra. The largest change in the phase angle occurred at frequencies between 1kHz and 100kHz. The largest changes in impedance magnitude occurred at frequencies below 10000Hz and increased by approx 25% over 1000 cycles. The exact frequency range of highest recorded change was different at different current densities but generally occurred below 50Hz. Because impedance magnitude increases as frequency decreases, the largest absolute changes always occurred at

frequencies below 50 Hz. Normalized impedance charts for all current densities are included in the full data set, see Appendix G for details.



Figure 7.21: Normalized (top) and Differential (bottom) impedance values for 0.4A/cm²

As shown in figure 7.22, changes in phase angle were less dramatic except at frequencies greater than 10 kHz. All changes in this frequency range are discussed in section 7.8.



Figure 7.22: Normalized phase angle as a function of frequency and thermal cycling

Since there was not a baseline run done for a sealing pressure of 350 PSI, it is not possible to conclude whether the increased damage is from thermal cycling at higher sealing pressures or simply due to running the cell at higher pressures. This will be an integral part of a continued investigation.

7.5: Thermal cycling Run 3: 30-90°C, measurements taken from bipolar plates

This experiment was performed to test the effects of temperature range on thermal degradation. It was hypothesized that hydration properties of Nafion may change significantly near the boiling point of water. This hypothesis was tested over 1000 cycles at a stack pressure of 120 kPa.

Thermal Cycling Run 3								
Stack		Anode		Cathode				
Temperature Cycled (°C)	30-90	Pressure (kPa)	150	Pressure (kPa)	150			
Number of Cycles	1000	Dewpoint (°C)	72	Dewpoint (°C)	72			
Stack Sealing Pressure (PSI)	120	Inlet Temp (°C)	80	Inlet Temp (°C)	80			
Cell Temperature (°C)	75	Stoichiometry	4	Stoichiometry	6			

Table 7.5. Experimental parameters for Thermal Cyching Kun	Table	7.5:	Experimenta	l parameters fo	r Thern	nal Cv	cling Ru	m 3
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Figure 7.23: Measured polarization curves for Thermal Cycling Run 3



Figure 7.24: Measured cell impedance as a function of current density and thermal cycling



Figure 7.25: Measured impedance data at 0.8A/cm2 as a function of thermal cycling

Results from the polarization curves show that, much like the run in section 7.3, performance below 0.8A/cm² did not change significantly with potentials after 1000 cycles being ±1% of initial values. At higher current densities the cell performance improved slightly.

The impedance results from this run are similar to those from section 7.3 as well. The majority of data points are within \pm 5%. Unlike section 7.3, there is no significant change in impedance magnitude between 10 and 1000Hz. Representative normalized data are presented in figures 7.26 and 7.27. All normalized results are available in the full data set, see Appendix G for details.



Figure 7.26: Normalized impedance values for 0.2A/cm²



Figure 7.27: Normalized phase angle values for 0.2A/cm²

The reason that normalized phase angle strays from a value of 1 between 10 and 1000Hz is likely due to an erroneous initial measurement. All following runs show the same pattern and have similar values.

7.6: Formation of Contact Resistance

The experimental runs listed above have been ordered for clarity, they were not run in the order they have been presented. The actual experimental order was 7.4,7.3,7.1,7.5,7.2. After the first test was run, it was found that a contact resistance of approximately $8 \times 10^{-5} \ \Omega \text{cm}^2$ had built up between the graphite plates and the current collectors. It was assumed that the cause was oxidation of the copper due to a slow leak allowing humidified gasses between the plates. However, the copper did not appear oxidized and even after scrubbing with emery paper, the contact resistance remained.

With copper oxidation eliminated as a source of the contact resistance, it was then assumed that the cause was due to the reactant gaskets binding in their holes and preventing solid contact between the bipolar plates and the copper collectors. The gaskets were exchanged for smaller replacements but the contact resistance remained. This was not a significant problem since both potential and impedance measurements could be made directly from the bipolar plates, "upstream" of the contact resistance, which simply became a resistive part of the DC load.

However, there was a side effect. The contact resistance, which increased from run to run, grew as large as $2x10^{-4} \Omega \text{cm}^2$ with an associated voltage drop of 0.2 to 0.25V at high loads. Coupled with the fact that the load bank would saturate at 0.1V, this meant that the load bank would saturate at cell potentials as high as 0.35 V and is the reason that the polarization curves obtained for much of the study do not reach potentials below 0.3V.

The true cause of the contact resistance was not found until an experiment to measure the effect of temperature on polarization performance was performed. The TEC arrays (and reactant gaskets) were removed in an attempt to remove the contact resistance since the cooling cart alone could be used to control cell temperature for the test. When the contact resistance remained, it was hypothesized that the problem was bipolar plates themselves. The hypothesis was confirmed when the contact resistance disappeared after the bipolar plates had been scrubbed with emery paper.

Results suggesting that thermal cycling leads to an increase in contact resistance are in agreement with results from other studies. As described in section 2.5.2, Giddey et al. found that increased ohmic resistance was due to "an increase in contact resistance between various stack components". However, they listed several possible sources of increased ohmic resistance ⁽²⁸⁾. EunAe et al. were more specific, stating that ohmic resistance was not attributable to an increase in proton conductivity of the PEM, but probably due to an increase in the contact resistances between electrodes and PEM and between electrodes and the flow field ⁽²⁴⁾

This is the first reported work that finds degradation of the bipolar plates as a degradation method for thermal cycling. This makes sense from a first-principles analysis since thermal expansion during cycling will cause cyclic loading on various stack components. If the cyclic loading were to damage the graphite, it is likely that more degradation would occur against the rigid copper collectors than against the spongy material of the GDL.

Unfortunately, because the contact resistance was somewhat reduced during handling of the bipolar plates between each experiment, and due to additional thermal cycling done while tuning the TEC control algorithms, it is impossible to determine the rate of contact resistance growth from available data. One avenue for further research on the subject would be to measure the growth in contact resistance as a function of number of thermal cycles for various types of graphite. The bipolar plates used in this study were made from resin-bonded graphite (specifications are included in appendix J) so the results cannot be generalized across all types of graphite plate. Finding a graphite composite that resists the formation of a contact resistance is one possibility for mitigating the effects of thermal cycling.

7.7: Assessment of Cell Damage

For all runs, the performance after thermal cycling was worse than before cycling. However, for the most part, this damage was recoverable and initial performance was regained after a reconditioning period ranging from 1-2 hours. Since real situations will not involve multiple thermal cycles without cell operation it is likely that recovery times for a single thermal cycle will be much shorter.

7.7.1: Effect of Stack Sealing Pressure

Of the three runs that underwent thermal cycling, only the one with increased stack sealing pressure received irrecoverable damage. Comparing the MEA cycled at higher stack pressure (left side of figure 7.28) with the one from run 7.5 (right side of figure 7.28) which underwent the same number of cycles at lower stack pressure one can see visible signs of GDL damage.



Figure 7.28: Comparison of visible MEA damage

The lines visible at the corner of the MEA on the left are cuts in the carbon paper caused by the flow field of the bipolar plates. The cuts are on both sides of the MEA cycled at higher stack pressure. A faint pattern of compression matching the flow field pattern could be seen on the right hand MEA when it was held properly to the light, but no visible cuts to the GDL were present.

These results suggest that higher stack sealing pressure leads to increased cell damage. As mentioned earlier in this section, thermal expansion causes variable loading during thermal cycling. From calculations in appendix D, the total thermal expansion over a temperature differential of 60° C would be approximately 5µm. This expansion would lead to further compression of the bladder Oring, and a slight increase in the pressure of the compressed air in the bladder. The increased force due to this compression was approximately 1.9 PSI on the membrane.

Fatigue failure due to variable loading is a function of both the midrange stress and the amplitude of the variable stress, as well as the number of cycles. Increasing the stack sealing pressure increases the midrange stress and can lead to fatigue failure after a significantly smaller number of cycles ⁽⁴⁷⁾. However, because there was not a baseline test done without thermal cycling at higher pressure, further testing is required to better understand the relationship between stack sealing pressure and thermal cycling damage.

7.7.2: Effect of Temperature Range

This set of experiments contained runs at a moderate sealing pressure of 120 PSI that covered two temperature ranges, 20-80°C and 30-90°C. In both cases all damage incurred was reversible. Further testing of different temperature ranges at either higher stack pressures, or to a larger number of cycles is recommended to better gauge the effect of maximum and minimum cycle temperature.

7.8: Relevant Frequency Ranges

This section is divided into two subsections: measurements below 10kHz and measurements above 10kHz. The reason for this is that measurements above 10kHz showed some erratic behaviour and hence have been treated differently than the rest of the measurements.

7.8.1: Frequencies below 10kHz

MEAs cycled at a moderate stack pressure of 120kPa did not incur any irrecoverable performance decreases from thermal cycling. The test that cycled temperature from 20-80°C had impedance changes at intermediate frequencies. The phase angle increased by a factor of 1.5-2 over 2000 cycles between frequencies of 10 and 100Hz. Additionally, there was a decrease in impedance magnitude of approximately 20% over 2000 cycles between 10 and 1000Hz. Thermal cycling is expected to increase cell impedance, not decrease it, which brings the validity of these results into question.

The test that cycled temperature from 30-90°C did not show any significant changes in either impedance magnitude or phase angle below 10 kHz.

7.8.2: Frequencies Above 10kHz

There are two separate factors that contributed to the erratic behaviour at these frequencies. The first was due to impedance readings by the FRA, which while repeatable, were clearly inaccurate. This is best explained by example. Phase angle measurements at 100 and 1000 cycles are shown in figure 7.29. There are two frequencies that have suspicious data points, 70-90kHz and 400-600 kHz.



Figure 7.29: Erratic high-frequency measurements

Examining figure 7.29, a small dip in phase angle is seen between 70-90kHz for both sets of measurements and a large dip occurs at 400-600 kHz for the measurement at 100 cycles but not at 1000 cycles. These dips are not due to spurious measurements; full spectra were repeated several times and the dips remained at the same frequency, and with the same values. However, when the next set of measurements was ready, hours or days later, the dips may or may not have reoccurred.

The most likely explanation for this behaviour is a source of noise in the building that was either present or not present depending on whether a piece of equipment was in use or not. These erratic measurements do not pose a large problem as this study is not concerned with measuring absolute values and, examining figure 7.25, it is possible to see past these measurements to determine general trends. However, they do pose a problem when normalizing data.

The second factor affecting high frequencies occurred between the 2^{nd} and 4^{th} run (sections 7.3, 7.1, and 7.5). The measurements from section 7.1 are too erratic to be useful, but the data from sections 7.3 and 7.5 shows an interesting trend. Shown in figure 7.26, the phase angle increases (a drop on the chart since the scale is negative) after the first measurement and then decreases with each successive measurement



a) b) Figure 7.30: High frequency phase angle measurements a) from Thermal Cycling Run 3, and b) from Thermal Cycling Run 1

In figure 7.30a, the change in phase angle began at the 100-cycle measurement. In figure 7.30b, the 1 cycle and 100 cycle measurements were nearly identical and the change began at the 250-cycle measurement.

This behaviour may be related to the contact resistance that was forming between the bipolar plates and the current collectors or it may simply be an artifact of the stack. Further study will be necessary to discern which is the case.

Chapter 8: Conclusions and Recommendations

New hardware was designed and constructed to allow in-situ diagnosis of the effects of thermal cycling on PEMFC performance using EIS. It was hypothesized that cumulative cell damage would be accompanied by corresponding cell impedance changes at different frequency ranges.

Unlike previous studies, EIS was applied using two separate loads. A static DC load drew the majority of the current from the cell while a smaller AC load was designed and manufactured to apply the periodic load required for EIS measurements.

Additional hardware was developed to allow accelerated thermal cycling of a single PEMFC cell. Equipment designed and manufactured specifically for this thesis includes: graphite bipolar plates and silicone gaskets required to form a single PEMFC cell; stainless steel manifold plates to act both as water jackets and to direct reactants and products to and from the cell; copper collector plates to gather the current generated by the cell; a pneumatic bladder and stack components required to allow variable compression of the cell; TEC arrays used in tandem with the water jackets to allow variable temperature control of the cell; and a switching mechanism to control the TECs. A software program was written using Labview to control the switching mechanism.

The cell was used to perform galvanostatic impedance measurements in situ. The measurements were made at 75°C and at four different current densities (0.2,0.4,0.6, and 0.8A/cm²) over the frequency range 1Hz to 1MHz. The applied sinusoidal current perturbation corresponded to $\pm 1.13 \times 10^{-2}$ A/cm², which kept changes in stack potential below ± 5 mV; this was smaller than the thermal voltage and allowed measurements to be considered linear. The gathered data represents the first reported set of measurements covering the frequency and current density ranges listed above.

Several conclusions can be drawn from the above data. The most significant of which is that EIS measurements can be made using a parallel loading approach. Measurements obtained were repeatable, showed trends in agreement with similar impedance measurements from published literature ^{(7), (12)(41)-(46)} and were of proper magnitude as confirmed by comparison to the slope of the polarization curve. By designing a small AC load bank to apply the periodic load, EIS can now be performed on real loads. This is an important step towards moving this non-intrusive diagnostic technique out of the laboratory and into practical situations.

From the preliminary data gathered, it appears that the main failure mode of thermal cycling is an increased contact resistance between the graphite plates and copper collector. This is in agreement with previous work by Giddey et al. ⁽²⁸⁾ and EunAe et al. ⁽²⁴⁾ who both cited an increase in contact resistance between various stack components as a possible failure mechanism. All potential measurements were made from voltage probes attached directly to the bipolar plates. This means that the magnitude and growth rate of the contact resistance (and associated voltage loss) was not directly measured in this study and is an avenue for further research. Beyond the increased contact resistance, thermal cycling between operational temperatures and ambient temperatures in the range of $20-30^{\circ}$ C did not have a significant effect on fuel cell performance at moderate stack sealing pressures. For experiments over 2000 cycles between 20 and 80° C and 1000 cycles between 30 and 90° C there was no irrecoverable performance degradation.

When sealing pressure was increased to 350 PSI, the average loss of potential varied with current density but peaked at 0.057 mV/cycle for 0.8A/cm². This suggests that stack sealing pressure is a significant factor to the amount of performance degradation. However, further baseline testing is required to ensure that the performance decrease is due to thermal cycling and not simply running the cell at higher pressures.

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A. Appendix A: Electrical Work and Gibbs Free Energy

The First Law of Thermodynamics states that energy is conserved, that is, it cannot be created or destroyed, simply changed between various states. The total internal energy of a closed system can be defined as:

$$U = q - w \tag{A.1}$$

where q is the heat input to the system and w represents work done by the system on its surroundings. An infinitesimal change in internal energy can be represented by the corresponding changes in heat and work:

$$dU = \overline{dq} - \overline{dw} \tag{A.2}$$

Note that internal energy is a state function in that U depends only on the state of the system, and not on the path or process followed to achieve that state. As the system changes from state 1 to state 2, the algebraic sum of q and w is fixed, though their individual values are not. Changes in internal energy are precisely given by the integral of (A.2)

$$\Delta U = \int_{U_1}^{U_2} dU = q - w \tag{A.3}$$

For fuel cell analysis, it is useful to separate work into electrical and mechanical contributions

$$dU = dq - dw_{e} - dw_{m} \tag{A.4}$$

where the reversible mechanical work is defined as:

$$w_m = -\int_{V_1}^{V_2} P dV \tag{A.5}$$

where P represents system pressure and V system volume. Other state functions pertinent to this analysis include Enthalpy, H, and Gibbs Free Energy, G, defined as:

$$H \equiv U + PV \tag{A.6}$$

$$G \equiv H - TS \tag{A.7}$$

where T represents temperature and S entropy. Using these definitions and equation A.4, the change in entropy for a system moving from state 1 to state 2 can be calculated as:

$$dH = dU + PdV + VdP = \overline{d}q - \overline{d}w_{e} - \overline{d}w_{m} + PdV + VdP$$
(A.8)

Using equation A.5, *dH* can be written as:

$$dH = \overline{d}q - \overline{d}w_e + PdV - PdV + VdP \tag{A.9}$$

For an isobaric process, dP=0 and dH reduces to

$$dH = \vec{d}q - \vec{d}w_a \tag{A.10}$$

From these results, the change in enthalpy can now be related to a corresponding change in G:

$$dG = dH - TdS - SdT \tag{A.11}$$

Combining with A.10,

$$dG = \overline{d}q - \overline{d}w_e - TdS - SdT \tag{A.12}$$

For a system at constant pressure and temperature, q = TdS and dT=0. Integrating dG using these constraints, the maximum obtainable work is simply

$$w_e = -\Delta G \tag{A.13}$$

This shows that the maximum electrical work that can be obtained from an ideal (isobaric and isothermal) fuel cell depends *solely* on the associated change in Gibbs Free Energy of the electrochemical reactions.

B. Appendix B: Engineering Drawings

Technical drawings were made for each of the components created for this work. The drawings were generated using Solidworks 3D modeling software and electronic versions of the relevant models were made available at the time of publishing and details of how to find them can be found in appendix G. This appendix serves as a reference guide to those files.



Insulating Pad



Air Side Bipolar Plate

88

.







Manifold Plate

<u>b</u>



Lower Manifold Plate



Base



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Bladder



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:

Bladder Cap

 $\mathbf{\Phi}$





D. Appendix D: Supporting Calculations

Heat Transfer Calculations for TECs

Find Heating and Cooling Load from Melcor Graphs Assume 50oC Cooling cart temp, halfway between 20oC and 80oC

Cooling, temp difference will vary between zero and 30oC, assume worst case, 30oC for full time. Assume 7Amps current

From chart, 30oC at 7Amps =	25W cooling per TECx12 TECs=	300W Cooling Load					
The heating load will be ohmic resis	tance under same conditions						
From chart, 7Amps corresponds to 7.2V at 30oC							
Therefore,	7Amps x 7.2V x 12 TECs	604.8W Heating Load					
Find Thermal Mass of System Assume water jackets stay at same is isothermal too	,						

Thermal Masses

Material	# plates	Area (m^2)	Width (mm)	Dens.(kg/m^3)	Cp(J/kgK)	DeltaT (K)		Therm. Mass (J)
Graphite	2	0.01	6.35	2210	700	60		11788.14
Copper	2	0.01	2.5	8900	400	60		10680
MEA	1	0.0025	0.25	1000	4200	60		157.5
							Total	22625.64

*Assume MEA thermal mass will be dominated by water and therefore approximate as same thermal properties

Find Heating and Cooling Times

Cooling:	Time = Thermal Mass/Cooling Load	<u>22626 J</u> 300W	75.4 seconds Cooling Time
Heating	Time = Thermal Mass/Cooling Load	<u>22626J</u> 604.8W	37.4 seconds Heating Time
		Total Cycle Time	113 seconds

This time does not include the effects of convective cooling from the stack, or contact resistances between various stack components. Assume final cycle time will be between 2-3 minutes

.

Hydraulic Diameter of Channel Depth = 3mn Channel Width =4mm	of Water Jacket Channel n		
	Dh=4xArea/Perimeter	<u>4(3mmx4m</u> (3mm+4mm+3mr	<u>m)</u> 3.43mm m+4mm)
Reynolds Number Assume Flow rate = 1 viscosity = 528x10-6	litre per minute/ 2 water ja	ckets = 0.5 l/min =	0.00833 kg/sec
Reynolds number =	<u>4xmass flow rate</u> PI x Diameter x visco	sity	= 5856.3 Therefore Turbulent
Nusselt Number Correlation for Nussel	t Number for turbulent inter	nal flow	
Nusselt = 0.023*(Rey	nolds number)^0.8 * (Prand	tle Number)^n	
n= 0.4 for heating, 0.3 Prandtle number ~ 3.4	for cooling 12 at 50oC		
Nusselt =	0.023*(5856)^0.8 * (3.42)^0).3	38.85410696 Nusselt
Convective Heat Tra <u>h = Nusselt x k</u> Diameter k=0.645	nsfer Coefficient (h) h = 34.4 * 0.64 0.00343	15 3	7306 W/m^2K h
Temperature Differe Heat Transfer = h x A Heat Transfer = 570 V Area ~ 0.005 m^2	nce for 570 W area x Temp Difference V / 2 plates = 285 W/plate		
Temp Difference = 28	5W / (0.005m^2 * 7306 W/r	n^2K)	7.8oC

Can the water jacket remove 605 W?

Therefore, the temperaure difference between the water jacket and TECs needed to dump the heat is 7.8 oC, this is a reasonable value

Polarization Slope Calculations

Chart of cell potentials								
Load (Amps)	Current Density		Ce	Il Potential	(mV)			
(Amps)	(A/cm^2)	1 cycle	100 cycles	250 cycles	500 cycles	1000 cycles		
0	0	976	980	973	975	973		
0.5	0.02	872	883	883	881	881		
1	0.04	854	855	854	854	854		
2	0.08	825	823	823	823	822		
5	0.2	762	757	760	758	758		
10	0.4	679	682	680	681	677		
15	0.6	605	601	605	604	599		
20	0.8	503	504	505	503	499		
24	0.96	390	388	394	399	386		
25	1	355	349	360	361	350		
26	1.04	312	300	325	312	310		
To find the appr and the slope fr	To find the approximate slope at 0.8 A/cm ² , look at the slope from 0.6-0.8 and the slope from 0.8-0.96 and average them							
Slope = rise/rur	1	·		۴				
for 1 cycle, the	slope between 0.8 a	nd 0.96A/o	cm^2 is: <u>(</u> 5	503-390)/100 (0.96-0.8)	1 <u>0</u>	0.70625 Ohms/cm^2		
the slope betwe	en 0.6 and 0.8 A/cm	י^2 is	<u>(6</u>	<u>305-530)/100</u> (0.8-0.6)	<u>10</u>	0.51 Ohms/cm^2		
Averaging the t	wo we get	(0.70625+	0.51)/2			0.608125 Ohms/cm^2		

The corresponding Average slopes at other cycle counts are:

Cycle #	1	100	250	500	1000
Approximate Slope (Ohms/cm ²)	0.608125	0.6175	0.589375	0.575	0.605625
Approximate Slope (Ohms/cm^2)	0.608125	0.6175	0.589375	0.575	0.6
Thermal Expansion Calculations

Assume that only the material between the water jackets expands. The water jackets are at constant temperature and will not change much overall.

Assume further that the TECs stay approx the same size since they are simply switching their hot and cold sides during operation

Therefore, the only materials that are thermally expanding are the copper collectors and graphite plates. Due to the thin nature of the MEA, it's change in size is neglected

Thermal cycle is 20-80oC or 30-90oC either way it's a 60o difference

Coefficient of Thermal expansion of copper (1/oC)	0.000016
Coefficient of Thermal expansion of graphite (1/oC)	0.000005
Thickness of copper collectors (mm)	2.5
Number of copper collectors	2
Thickness of graphite plates (mm)	6.35
Number of graphite plates	2

Thermal expansion = coefficient of thermal expansion x thickness x number of plates x temp difference

0.000016x2.5x2x60 + 0.0000005x6.35x2x60

0.00000495 thermal expansion (m)

The thermal expansion will lead to compression of the softest member, in this case Oring the pneumatic bladder

Oring width (inches)	0.275
Oring width (mm)	6.985
Oring ID (mm)	75
Oring OD (mm)	88.97

the Oring compression is 0.000005m / 0.007m

Oring Compression

For an Oring with a Shore A hardness of 70, a 10% compression (between 20-30%) is 500lb per linear inch of seal (see graph on next page)

Therefore, a compression of 0.071% is

 500 x 0.00071
 0.35 pounds per inch of seal

 Length of seal is the circumference of the Oring =

 Mean circumference(mm) = 75+ 89 /2
 82

 Circumference (inches)
 10.14214951 inches

 Total force on Oring
 3.593675024 pounds

 The GDL area is 4 square inches therefore
 0.898418756 PSI on membrane

7.09E-04

The compression of the bladder will also lead to higher pressure in the compressed air.

From simplification of the ideal gas law:	P1*V1 = P2*V2
Therefore, the new pressure P2 will be	P2 = P1*V1 / V2
Because the area of the bladder doesn't change, only the height:	P2 = P1 * X1/X2

Nominally, X1, the clearance between the bladder and bladder cap is 2 mm, this will vary slightly depending on the exact compression of the Oring, but is a good starting point for this calculation X2 will be X1 minus the thermal expansion of 0.005 millimeters

Therefore, P2 = P1 (100 PSI) * 2mm / (2mm-0.005mm) The pressure difference is therefore 100.2506266 0.250626566

And the pressure on the membrane will be

1.002506266 PSI

The total added pressure to the membrane will be 1.9 PSI

5700 Handbook Parker O-Ring Handbook





Figure 2-8: .275 Cross Section

E. Appendix E: Cell Conditioning

This appendix gives relevant stack data obtained during an 11.5-hour cell-conditioning run. The time difference between cells varies and the time each measurement was taken is displayed in the first column. Notice that the cell is not conditioned at a single load. Performance increases, in the form of increased potential, at a given current density quickly level off. By varying between several loads, the leveling off occurs at progressively higher voltages.

Notice also the occasional "pushes" where current density is increased until cell voltage dropped below 0.2V (in this test this happened at 1:02, 1:45, 2:50, 5:00, 5:43, and 7:47). It was found that this helped improve conditioning at higher current densities. Another strategy that seemed helpful was dropping the cathode flow rate until cell potential dropped to zero. When the cathode flow rate was restored, the cell potential increased above previous levels. This technique has diminishing returns when used many times.

Time	Load	Current	Potential	Reactant	Cathode	Anode	Stack	Cathode	Anode	Cathode Dew	Anode Dew
		Density		Pressure	Flow Rate	Flow Rate	lemp	Inlet I emp	Inlet I emp.	Point Temp.	Point Temp.
	Amps	A/cm ⁻	V	kPa	nmlpm	nmlpm	°C	°C	°C	°C	ъс
9:13:15 AM	0	0	0.013	0.5	8.636	0.717	22.5	21.1	20.6	20.8	21.3
9:13:45 AM	0	0	0.198	2.7	411.743	192.177	22.6	21.1	20.6	20.8	21.3
9:14:15 AM	0	U	1.035	5.7	411.743	203.873	23.2	21.7	20.9	21	21.3
9:14:45 AM	0	0	1.024	35.7	416.229	204.674	24.5	27.4	23.1	21.5	21.4
9:15:15 AM	0	0	1.038	31.7	416.87	204.033	26.4	32.6	29.1	22.2	21.7
9:15:45 AM	0	0	0.724	30.7	418,793	201.149	28.7	39.5	35.1	23.3	22.3
9:16:15 AM	0	0	0.778	30.2	418.793	197.945	31.3	49.2	41.4	25.6	23.1
9:17:15 AM	0	0	0.776	30.2	418.152	205.315	35.9	65.5	55.7	34	26.1
9:18:15 AM	0	0	0.773	30.3	419.434	203.072	41.1	74.9	69.5	47.4	31.2
9:19:15 AM	0	0	0.955	30	420.074	200.027	46.9	78.1	74.7	58.9	38.6
9:20:15 AM	0	0	0.961	30.7	420.074	200.989	49.4	78.9	75.2	61.1	42.3
9:21:15 AM	0	0	0.953	30.1	445.709	200.668	57.4	81.3	86.4	70.1	58.8
9:22:15 AM	0	0	0.945	29.9	427.124	196.983	61.5	81.4	86.8	72.7	67.2
9:24:15 AM	0	0	0.932	153.9	433.533	201,309	66.4	85.3	83.2	74.5	68.7
9:26:15 AM	1	0.04	0.777	149.3	416.87	202,911	67.4	88.6	84.4	75.1	77 1
9:28:15 AM	0.6	0.024	0.663	150 1	515 564	136 902	68.6	83.6	86.2	74.5	80.1
9:30:15 AM	04	0.016	0 496	1497	1320 496	365 532	71.2	87.4	84 7	73.3	77.8
9:32:15 AM	0.4	0.016	0.492	149.2	1217 316	335 732	72.6	81.6	84.5	72.9	72.0
0:34:15 AM	0.4	0.016	0.488	140.2	1119 622	300 456	72.6	927	95.6	72.5	72.5
0:36:15 AM	0.4	0.010	0.496	140.7	1067 252	209.430	74.0	03.7	00.0	72.0	70.4
9.30.15 AM	0.4	0.016	0.480	149.7	1007.332	290.241	74.2	0/	00.1	72.7	72.1
9.30.13 AM	0.4	0.010	0.484	150.0	1023.773	201.097	74.4	03.9	04.7	72.1	73.4
9.40.15 AM	0.4	0.016	0.482	150	1006.47	274.529	74.2	84.9	85.1	73.7	73.8
9:45:15 AW	10	0.4	0.475	150.4	1014.16	281.418	73.8	88.8	84.9	/4.4	76.1
9:45:45 AM	10	0.4	0.473	150	1019.928	281.738	73.8	87.5	84.9	74.5	75.8
9:50:15 AM	10	0.4	0.457	149.2	1019.928	280.457	74.1	84.8	85	74.3	73.4
9:55:15 AM	10	0.4	0.502	150.1	1021.21	282.219	74.3	84.7	84.9	74.5	75.7
10:00:15 AM	10	0.4	0.518	149.6	1014.16	282.059	74.2	84.6	84.9	74.2	72.9
10:05:15 AM	10	0.4	0.531	150	1022.491	283.02	74.5	84.7	84.9	74	74.4
10:10:15 AM	10	0.4	0.534	149.9	1027.618	283.821	74.4	85	84.9	74.1	74
10:15:15 AM	10	0.4	0.536	150	1018.646	281.578	74.4	84.6	85	74.3	74
10:20:15 AM	10	0.4	0.536	149.8	1013.519	281.097	74.4	85	85	74	74.1
10:25:15 AM	10	0.4	0.545	149.9	1023.132	281.418	74.4	85.2	84.9	73.6	74
10:30:15 AM	10	0.4	0.548	150.2	1030.823	283.02	74.4	84.7	84.8	74.2	73.9
10:35:15 AM	10	0,4	0.546	150	1012.238	282.7	74.4	85.2	85	74.1	73.9
10:40:15 AM	10	0.4	0.551	150	1019.287	280.937	742	84.6	85	74 1	74 3
10:45:15 AM	10	0.4	0.553	150	1019.928	280 777	74.2	84.9	85 1	74.2	73.9
10:50:15 AM	10	0.4	0.557	150.2	1014 801	279 976	74 1	84.9	85	74.1	74
10:55:15 AM	15	0.6	0.487	149.8	1515 961	420 647	75.5	80	84.9	74.1	73.0
11:00:15 AM	15	0.0	0.503	140.0	1520 447	420.047	75.4	84	84.0	74.1	73.9
11:05:15 AM	20	0.0	0.303	149.9	1520.447	420.007	73.4	04	04.9	74	74
11:10:15 AM	20	0.0	0.330	150.2	1506.045	420.400	77.0	00.4	00	13.9	74.1
11.10.13 AIVI	20	0.0	0.31/	150.3	1520.215	420.893	77.0	05.2	05	73.9	74.2
11.15.15 AM	20	0.0	0.334	150,1	1024.933	422.729	0.11	85.1	85	74.1	74.1
11:20:15 AM	20	0.8	0.336	150.1	1522.369	420.647	11.1	85	85	(4	/4
11:25:15 AM	20	0.8	0.342	150.3	1527.496	422.569	//.7	85	85	74.2	74.7
11:30:15 AM	20	0.8	0.341	150	1525.574	422.089	77.8	85.3	84.9	73.4	73.8

Time	Load	Current	Potential	Reactant	Cathode	Anode	Stack	Cathode	Anode	Cathode Dew	Anode Dew
		Density		Pressure	Flow Rate	Flow Rate	Temp	Inlet Temp	Inlet Temp.	Point Temp.	Point Temp.
	Amps	A/cm ²	V	kPa	nmipm	nmlpm	°C	°C	°C	°C	°C
11:35:15 AM	20	0.8	0.352	149.9	1524.292	420.326	77.8	85.1	85	74.2	74.1
11:40:15 AM	20	0.8	0.344	149.9	1522 369	420 807	77.8	84.8	85	74.2	74 1
11.45.15 AM	20	0.8	0 344	150.1	1517 883	419 685	77.8	85	85	74.1	74.1
11:50:15 AM	20	0.8	0 345	150.1	1517 242	422.089	77.8	85	85.1	74.1	74
11:55:15 AM	23	0.02	0.040	150.1	2320 802	644 15	79.4	82.0	84.9	74.1	720
12:00:15 PM	20	0.92	0.21	150.5	1520.092	416 060	70.4	02.9	04.0	74.1	73.9
12.00.15 FM	20	0.0	0.301	150	1530.06	410.902	77.7	04.1	64.9	74	73.9
12:10:15 PM	22	0.88	0.297	150.1	16/2.9/4	462.784	77.8	85.3	84.9	74.5	74
12:20:15 PM	20	0.8	0.391	150.1	1519.165	420.166	77.7	85.4	84.9	74.1	74
12:30:15 PM	20	0.8	0.416	150.3	1524.292	418.243	77.5	81.7	85.1	73.7	73.6
12:40:15 PM	20	0.8	0.405	150.2	1516.602	421.928	77.4	85.3	85	74.5	74.4
12:50:15 PM	20	0.8	0.402	149.8	1529,419	417.282	77.5	84.7	84.9	74.4	73.9
1:00:15 PM	20	0.8	0.401	149.9	1514.679	424.011	77.4	84.8	85	74.1	74
1:00:45 PM	20	0.8	0.376	150.1	1517.883	421.928	77.4	85	84.9	74.1	74.1
1:01:15 PM	20	0.8	0.403	150	1522,369	421,288	77	85	84.9	74 1	74
1.01.45 PM	20	0.8	0.396	149.9	1527 496	419 685	77 3	84.9	84.9	74.1	74
1:02:15 PM	23	0.02	0.200	150.5	1740 906	483.612	77.7	85.6	95	74.1	74 1
1:02:45 DM	20	0.92	0.233	150.5	1822.200	403.012	79.0	86.0	00	74.2	74.1
1.02.45 FM	24	0.90	0.227	150.8	1022.290	030.002	70.2	00.2	05.1	74.1	74.2
1.03.15 PM	24	0.96	0.255	150.7	2418.945	6/1.867	78.2	87.7	85.4	73.9	(4.4
1:03:45 PM	25	1	0.19	150.5	2512.512	/01.02/	78.4	87	85.3	74.2	74.3
1:04:15 PM	15	0.6	0.535	148.1	1515.32	420.647	77.6	83.1	84.8	74	74.1
1:10:15 PM	15	0.6	0.515	149.6	1139.13	317.627	75.7	83.8	84.9	74.1	74.3
1:20:15 PM	15	0.6	0.536	149.9	1515.961	421.768	75.7	85	85	73.8	73.9
1:30:15 PM	15	0.6	0.531	149.8	1526.215	423.851	75.7	85	85	74.1	74.2
1:40:15 PM	15	0.6	0.532	149.9	1530.701	420.326	75.7	85.3	84.9	73.4	73.6
1:40:45 PM	15	0.6	0.533	149.9	1507.629	420.647	75.7	85	84.9	73.5	73.3
1:41:15 PM	15	0.6	0.534	150.1	1521,729	422,729	75 7	85.1	85	73.1	73
1.41.45 PM	20	0.8	0.435	150.1	1517 883	422 409	75 7	85	85.1	73.6	73
1:42:15 PM	20	0.8	0.406	150.1	2021 606	561 317	76.2	86.8	85.3	73.0	735
1:42:45 DM	20	0.0	0.400	150.5	2021.000	560.070	76.2	80.0	05.5	73.9	73.5
1.42.45 FW	20	0.0	0.409	150.5	2013.190	502.279	76.5	00.3	05.3	74	74.1
1.43.15 PW	20	0.8	0.411	150.5	2010.071	004.00Z	76.7	85.4	85.2	74.2	74.7
1:43:45 PM	20	0.8	0.409	150.1	2012.634	566.605	76.8	84.4	85	73.8	75.1
1:44:15 PM	24	0.96	0.347	150.4	2219.635	616.913	77	84.3	85	74.4	75.5
1:44:45 PM	24	0.96	0.262	150.4	2417.664	674.911	77.5	85	85	74.5	75.7
1:45:15 PM	24	0.96	0.255	150	2408.051	672.028	77.9	85	85	74.4	75.6
1:45:45 PM	25	1	0.202	150.2	2508.026	698.463	78.2	84.8	85	74.4	75.4
1:46:15 PM	20	0.8	0.411	148.7	2010.712	563.721	78.1	83.9	84.9	74.3	75.1
2:00:15 PM	20	0.8	0.413	150	2019.043	564.682	77.4	84.9	84.8	74	74
2:15:15 PM	20	0.8	0.416	149.9	2005.585	564.041	77.3	85	85.1	74	74
2:30:15 PM	10	0.4	0.641	149.8	1015 442	281 418	74.6	85.1	84 7	74 1	73.8
2 45 15 PM	10	0.4	0.631	150	1013 519	282.86	74.5	84.8	85	74.1	74.1
2:45:45 PM	10	0.4	0.627	149 7	1017 365	282.00	74.5	84.8	85.1	74	74.1
2:46:15 DM	10	0.4	0.027	140.0	1010.303	202.7	74.5	04.0	00.1	72.0	74.1
2.40.13 FW	00	0.4	0.03	149.9	1019.207	201.730	74.5	04.1	65	73.0	74
2:46:45 PW	20	0.8	0.426	150.4	2018.402	563.4	/5.4	90,7	85.5	73.1	(4.1
2:50:45 PM	24	0.96	0.297	150.8	2386.902	667.221	77.2	83.1	84.9	74.5	75.3
2:51:15 PM	25	1	0.275	150.2	2511.23	701.027	77.7	84.3	85.2	74.6	75.6
2:51:45 PM	25	1	0.276	150.5	2516.357	702.469	77.9	84.7	85.3	74.5	75.5
2:52:15 PM	20	0.8	0.419	149.3	2001.74	568.687	77.8	84.6	85.2	74.5	75.2
2:52:45 PM	20	0.8	0.425	149.7	2014.557	562.119	77.2	83.4	85	74.5	74.9
3:00:15 PM	20	0.8	0.428	150.1	2010.071	563.881	75.4	85.1	85	74.1	74
3:10:15 PM	20	0.8	0 439	150.5	2020 325	564 041	76	84.9	85	74.1	74
3.20.15 PM	20	0.8	0 4 2 4	150	2006 226	562 759	75.9	85.1	85	73.8	7/ 1
3:30:15 PM	10	0.0	0.424	150 1	1021 21	282.050	73.5	94.0	05	73.0	74.1
3.30.15 FW	10	0.4	0.047	150.1	1021.21	202.059	73.3	04.9	65	74	74.3
3:40:15 PM	10	0.4	0.64	149.9	1023.773	281.738	/3.1	85.1	85	74.1	74.2
3:50:15 PM	10	0.4	0.638	150	1021.851	282.86	73	84.8	85.1	74.2	74.1
4:00:15 PM	10	0.4	0.635	150.1	1021.851	280.777	73	85	85	74.4	76.1
4:10:15 PM	10	0.4	0.633	149.8	1023.132	282.059	73	85.1	84.9	74	73.9
4:20:15 PM	10	0.4	0.631	150	1021.21	282.7	73	85.2	85	74	74.2
4:30:15 PM	10	0.4	0.633	150.2	1021.21	281.898	73	85.1	85	74.1	74.1
4:40:15 PM	20	0.8	0.428	149.4	2017.761	563.4	75	85.7	85	74.1	74 1
4:50:15 PM	20	0.8	0.446	150	2018 402	565,804	75 5	85.2	85	74	74
5:00:15 PM	20	0.8	0 444	150.8	2013 275	562 / 30	75 /	85 /	85.2	73.1	73 5
5:06:15 DM	20	0.0	0.444	150.0	2013.273	562 500	75 9	00.4	00.2	73.1	13,0
5.00.10 FW	20	0.0	0.440	150.1	2013.275	302.399	13.3	65	00	74.4	15.4
5:00:45 PM	24	0.96	0.344	150.8	2420.227	0/1.38/	/5.6	85.9	85.2	74.3	/5.1
5:07:15 PM	27	1.08	0.212	151.2	2815.002	/85.622	/6.3	87.1	85.7	74.3	74.7
5:07:45 PM	20	0.8	0.451	147.6	2006.226	565.804	76.4	85.2	85.2	74.3	74.3
5:10:15 PM	10	0.4	0.652	147.4	1019.928	279.816	74.9	82.8	84.4	74	73.6
5:15:15 PM	5	0.2	0.74	150	518.768	142.99	72.2	81.2	84.7	74.1	73.9
5:20:15 PM	5	0.2	0.733	149.6	512.36	142.189	71.6	84.7	85.2	73.7	74.2
5:30:15 PM	20	0.8	0.431	150.5	2010.712	561.157	75.3	84.9	85	74.1	74.1
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Time	Load	Current	Potential	Reactant	Cathode	Anode	Stack	Cathode	Anode	Cathode Dew	Anode Dew
		Density		Pressure	Flow Rate	Flow Rate	Temp	Inlet Temp	Inlet Temp.	Point Temp.	Point Temp.
	Amps	A/cm ²	V	kPa	nmlpm	nmlpm	°C	°C	°C	°C	°C
5:41:45 PM	19.7	0.788	0.456	150.2	1983.795	554.749	75.2	84.8	85	74	73.9
5:42:15 PM	19.7	0.788	0.463	150.7	1995.331	557.152	75.2	84.8	85.1	74	73.8
5:42:45 PM	24	0.96	0.337	151	2415.741	673.63	75.5	85.8	85.1	74	73.9
5:43:15 PM	27	1.08	0.889	150.4	2681.061	746.208	75.9	86.1	85.2	74	74.1
5:43:45 PM	26	1.04	0.273	150.7	2629.791	725.7	76	86	85.3	74	74
5:44:15 PM	27	1.08	0.232	150.5	2721.436	757.423	76.5	85.6	85.3	74	74.1
5:44:45 PM	19.7	0.788	0.451	147.7	2012.634	562.92	76.6	83.8	84.9	74	74
5:45:15 PM	19.7	0.788	0.469	149.7	1976.105	554.909	76.2	82.6	84.7	74,1	74
6:00:15 PM	19.7	0.788	0.456	150.1	1998.535	552.025	75.3	85	84.9	72	72
6:10:15 PM	19.7	0.788	0.462	150	1995.331	555.389	75.2	85	84.9	72.1	72.1
6:20:15 PM	19.7	0.788	0.451	149.8	1992.767	553.947	75	85	84.9	72.5	73
6:30:15 PM	19.7	0.788	0.453	149.9	1976.746	555.229	75.1	85.1	84.9	72	72.3
6:40:15 PM	9.7	0.388	0.655	150	983.398	273.888	74.1	85.7	85.1	72	71.8
6:50:15 PM	9.7	0.388	0.648	149.8	993.011	273.087	74	85	85	72	72
7:00:15 PM	9.7	0.388	0.644	150.1	993.652	275.49	73.9	84.9	85	72	72
7:10:15 PM	9.7	0.388	0.641	149.8	994.934	275.33	74	85.2	84.9	72	71.9
7:20:15 PM	9.7	0.388	0.638	150	1000.061	271.645	73.9	85	85	72.1	71.9
7:30:15 PM	9.7	0.388	0.639	149.9	984.68	274.368	73.9	85	85	72	72.1
7:40:15 PM	19.7	0.788	0.437	150	1997.253	553.947	75.7	88	85.1	72.1	72.3
7:46:15 PM	19.7	0.788	0.447	150.4	2483.673	554.749	76	85.6	85.2	72.1	72
7:46:45 PM	25	1	0.283	151.8	3136.078	701.988	76.4	85.8	85.4	72.1	72.1
7:47:15 PM	25	1	0.255	150.3	3116.852	701.347	76.9	85.4	85.4	72.1	72.2
7:47:45 PM	25	1	0.223	150	3129.028	699.104	77.3	84.2	85.1	72.1	72.2
7:48:15 PM	20	0.8	0.391	146	1520.447	423.531	77.1	80.5	84.7	71.8	72
7:48:45 PM	20	0.8	0.412	148.8	1519.165	419.365	77.1	79.2	84.4	72	71.9
7:49:15 PM	20	0.8	0.418	149.9	1513.397	422.089	,77.1	81.1	84.3	72	71.7
7:49:45 PM	20	0.8	0.429	150	1524.292	423.21	77.1	83.6	84.5	72.1	71.8
7:50:15 PM	20	0.8	0.423	149.7	1520.447	419.685	77.1	86.4	84.8	72	72
8:00:15 PM	25	1	0.289	150.2	2505.463	701.988	75	85.6	85.4	72.1	72.2
8:10:15 PM	20	0.8	0.448	149.3	2021.606	562.599	76	84.1	84.6	72	71.9
8:20:15 PM	20	0.8	0.445	150.2	2013.916	561.157	75	84.8	85.1	72	71.9
8:30:15 PM	20	0.8	0.445	149.6	2020.325	558.914	75	84.9	85.1	72	72.1
8:40:15 PM	20	0.8	0.448	149.8	2031.219	561.157	74.9	85	85.1	72	72.2
8:40:45 PM	20	0.8	0.456	150.6	2024.17	564.842	74.9	84.9	85	72	72.1
8:41:15 PM	20	0.8	0.44	150.1	2003.021	562.439	74.9	85	85	72	72
8:41:45 PM	20	0.8	0.457	151.1	2006.226	563.4	74.9	84.9	85	72	72
8:42:15 PM	20	0.8	0.44	150	1998.535	561.157	74.9	85	85.1	72	71.9
8:42:45 PM	20	0.8	0.448	149.8	2001.74	561.798	74.9	85	85	72	71.7
8:43:15 PM	20	0.8	0.448	150.6	2012.634	562.119	74.9	84.9	85	72	71.8
8:43:45 PM	20	0.8	0.437	150.7	2009.43	562.279	75	84.8	85	72.1	72
8:44:15 PM	20	0.8	0.451	149.8	1995.972	561.638	75	84.9	85.1	72	72
8:44:45 PM	20	0.8	0.451	149.7	2010.071	566.605	75.1	85.1	85.1	72	72
8:45:15 PM	20	0.8	0.449	149.8	2005.585	563.881	75.1	85	85	72	72

F. Appendix F: Preliminary Experiments

Two preliminary experiments were run using only the cooling cart before the TEC Arrays were completed. The runs only went to 400 cycles due to the higher cycle time. Results are not valid since it was determined that the experimental procedure used was introducing outside sources of cell damage but the data is included here since it shows EISs ability to detect large changes in impedance spectrum for a small change in cell voltage output



The top two charts show data for 0.2 A/cm² and the bottom two show data for 0.4 A/cm². All data obtained was at 75oC, 200 kPag, with stoichiometries of 4 and 9 for the anode and cathode respectively.



Data for MEA 1, top row is 0.6A/cm², second row is 0.8A/cm². All data obtained was at 75oC, 200 kPag, with stoichiometries of 4 and 9 for the anode and cathode respectively.



Data for MEA2, 0.2A/cm². All data obtained was at 75oC, 200 kPag, with stoichiometries of 4 and 9 for the anode and cathode respectively.



MEA 2: Top row 0.4A/cm², middle row 0.6A/cm², bottom row 0.8 A/cm². All data obtained was at 75oC, 200 kPag, with stoichiometries of 4 and 9 for the anode and cathode respectively.

G. Appendix G: Obtaining the Full Data Set

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A complete data set including all impedance measurements and graphs, as well as stack operating conditions was submitted in electronic form (on CD) along with this thesis to the Faculty of Graduate Studies library at the University of British Columbia.

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H. Appendix H: Future Work

The steps to continue this project for thermal cycling are fairly straightforward.

- Repeat the procedure outlined in this thesis but make potential measurements (by hand using a multimeter) both from the copper collectors and directly from the bipolar plates to measure the contact resistance
- Scrub the bipolar plates with emery paper to remove the contact resistance between experiments
- Give extra attention to the frequency ranges listed as deserving more detail
- One of the biggest problems with the switching mechanism is that, in the case of a power shutdown, the DAQ system will restart and labview will no longer be controlling the TECs. In this case the TECs will likely overheat and damage themselves and the stack. Buying or building a mechanism to cut power to the switching unit in the case of a blackout is highly recommended. This way the equipment can be left to run overnight.
- The Greenlight test stand has been modified to use compressed air to power the backpressure valves instead of nitrogen. However, in this configuration it will leak air while not in operation. This was countered by simply unplugging the air line from the manifold on the laboratory wall while not in use

Implementing the mechanical cycling

Much of the work has been done to use EIS to measure the effects of mechanical cycling on the cell. Here's what's left to be done:

- The pump and motor to be used for pressure cycling have been sized and acquired. They are currently in Lab 270A above the DAQ system. Tubing, valves, fittings and a hydraulic reservoir have been acquired and can be found in 270A. Diagrams of the hydraulic system can be found in workbook #2
- The pump has been modified by removing 2 internal pistons. The actuators are currently wrapped in oiled towels and stored in lab 270A
- The stack bladder must be redesigned. Currently pressure in the bladder represents ¹/₄ the pressure on the MEA. This fact was neglected during pump sizing and the bladder must be redesigned with ¹/₄ the area or pressure on the MEA will be ridiculously high
- Hydraulic fluid and a hydraulic filter still need to be purchased. The loop was designed to be used with fire-retardant 95-5 fluid

I. Appendix I: FRA Settings

To properly reproduce these experiments, or perform similar ones, the Z-plot software should be setup as shown in figure I1:

器 ZPlot - Zplot for cor	nductivity Jan12_05.;	zp w (1260)	
<u>File Setup Measure H</u>	<u>t</u> elp		
	1 🖬 Z		Z 2 ?
Ctrl I: Sweep Freq	Ctrl I: Sweep DC	Ctrl I: Sweep Ampl	Ctrl I: Vs. Time
Ctrl E: Sweep Freq	Ctrl E: Sweep DC	Ctrl E: Sweep Ampl	Ctrl E: Vs. Time
Polarization: DC Potential (Volts) AC Amplitude (mV) Monitor: Off	0.6 Applied E		
Frequency Sweep:			
Initial Frequency (Hz)	E6 C	Linear 💽 Logarithmic	
Final Frequency (Hz)	0	iteps/Decade 💌 Inter	val 10

Figure I1: Z-plot screenshot

It is important to select the *Ctrl E: Sweep Freq* tab so that you can enter the relevant applied potential and frequency information. DC potential is measured in Volts while AC potential is measured in mV RMS.

To ensure that the FRA is properly communicating with Z-plot, select the setup menu (top left), which brings up 3 options: setup Z-plot; setup instrument, setup cell. Choose setup Z-plot to bring up the following screen (figure I2).

Setup ZPlot	×
Analyzer:	
Type Solartron 1260	F
GPIB Board 0 🗲 GPIB Address 6 👤	
Pstat/Gstat or Interface:	
Type 1260 StandAlone	•
Multiplexer: Type None	•
GPIB Board 0 🗲 GPIB Address 2 🗲	
Iest Gpib Data File Format: C ZPlot 1.x C ZPlot 2.3	
OK Cancel <u>H</u> elp	

Figure I2: Setup Z-plot menu

Ensure that the proper FRA is selected from the *Analyzer* menu; in this case a Solartron 1260. Under *Pstat/Gstat or Interface* choose 1260 standalone (note, if you have chosen a Solartron 1255, this option will become 1255 standalone). Under *Multiplexer* select none.

To check whether the equipment is connected properly or not hit the *Test Gpib* button at the bottom left. Hit the *OK* button to return to the main menu.

Another option from the *setup* menu on the main screen is *setup cell*. This menu is best left to its default values, but if you fear they have been changed, figure I3 shows the values as they should appear.

Electrode:	Polarity Convention
Surface Area (cm²)	Potential: Current:
Density (g/cm²)	C (02+) C (02+)
Equivalent Weight (g) 0	
Stern-Geary Coef. (mV) 26	Corrosion Units: MPY C mmPY
Reference Electrode Correction	on:
Reference Type User Defined	
Mue MHE	

Figure I3: Setup Cell Menu

The final option in the setup menu is *Setup Instruments*, which has two options itself. The first of which is *Analyzer* shown in figure I4.

etup Instru	ments (Solartr	on 1260)			
Measure 4	Analyzer				
Mode: C Gain Ph Source	nase C Group De ce V1 / V2	elay ি Impedance	Integration: Auto Integration Integration Tim Delay Tim	on Off e © <u>Seconds</u> e © Seconds®	Cycles 2 Cycles 0
Connectio	ons: Range	Coupling	Input	Outer	Location
V1(Ch.1)	Auto	DC 💌	Differential 💌	Floating 💌	NA
V2(Ch.2)	Auto	DC 💌	Differential 💌	Floating	NA
	I (Current)	DC 💌			Error Beep
			ОК	Cancel	Help

Figure I4: Analyzer Menu

Under *Mode* select the impedance button and V1/V2 from the pull down menu. These experiments were done with Auto Integration off under the *Integration* section. However,

Integration Time of 2 seconds or 50 cycles was chosen, telling Z-plot to average measurements taken over either 2 seconds or 50 cycles, depending on which is selected. Ensure that all options under the *Connections* section appear as they do in figure I4.

The final option is the *I Measure* tab on the *Setup Instruments* menu. Ensure that all current ranges appear as shown in figure I5.

Setup Instruments (Solartron 126	0)	×
I Measure Analyzer Current Ranges: High Frequency Low Frequency Auto Auto Minimum	Transition Frequency 5000	
Nulling Files: Short Open		
	OK Cancel He	lp

Figure I5: *I Measure* tab

APPENDIX J: GRAPHITE PLATE SPECIFICATIONS

1

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PEM – 501- 06- HS Graphite Plate

J. Ash Content and Physical Properties									
Ash Content	Porosity	Density	Electrical Resistivity	Tensile Strength	Hardness				
(%)	(%)	(g/cm ³)	(μ.Ω.m)	(MPa)	(Shore Scleroscope)				
0.001	0.59	1.95	9	49.8	52				

,

Custom Dimensions:

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Length: 10cm Width: 10cm Thickness: 6mm

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