Identification and analysis of key factors affecting performance of PEM fuel cell

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NANYANG TECHNOLOGICAL UNIVERSITY**

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NANYANG TECHNOLOGICAL UNIVERSITY**

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Summary

Analysis of PEM Fuel Cell performance was conducted by implementing two in-situ non destructive electrochemical assessment methods namely Current Measurement Method and Electrochemical Impedance Spectroscopy. In addition, two novel approaches were introduced to these two basic methods to identify key factors affecting the performance of PEM Fuel Cell. In the first approach, segmented fuel cell was used to assess Parallel, 1-S, and 3-S flow field topologies. The result revealed that topology design affects the cell performance and its distribution over the cell area significantly. Observation of the segment responses on the application of different cell potential (at the range of OCV–0.5 Volt) showed that in the absence of flooding, different parts of the cell undergo similar mechanisms but of different extent.

The second approach, Thin Film-Agglomerate Model, was used to differentiate the mechanisms occurring within oxygen and air cells. Both cells experienced performance limitation originating from Faradaic reaction, oxygen diffusion at agglomerate region, and diffusion at thin film region. The appearance of further diffusion limitation in the backing layer exhibited only by the air cell explained the difference between the performance of oxygen and air cell.

The last part of this project was devoted to investigate the effect of water management-related factors which is one of the key issues in the performance degradation of the PEMFC. The results showed that reactants humidification (especially at the anode-fuel side) increases the cell performance due to higher water content for higher ionic conductivity of Nafion. Application of back pressure in general leads to higher utilization of the catalyst surface active area and more water condensation for improved proton conductivity.

Introduction

1.1. Background

Application of Polymer Electrolyte Membrane Fuel Cell (PEMFC) for land vehicle, portable, and stationary power generation purpose has increased in recent years as it has become more competitive as an alternative energy converting system. PEMFCs can be used in all fields where the well-developed Internal Combustion Engine (ICE) is applied with the additional advantage of higher efficiency compared to the ICE. In addition to that, the PEMFC has minimum or no moving parts and its power capacity can be increased easily by adding more cells into a stack, offering expandable and flexible supply of electricity.

PEMFC can be defined as one type of electrochemical device capable of converting chemical energy contained in fuel and oxidant directly into electricity with the aid of an electrocatalyst. As the name implies, this system uses polymer electrolyte membrane (also known as proton exchange membrane) as its electrolyte. The choice of the electrolyte will eventually affect the fuel cell operating condition. In PEMFC, this leads to the strong characteristics of this type of fuel cell – its capability to deliver power at room temperature (optimum at 80°C) with fast load response, and fast start up. Utilizing a solid polymer membrane, little problems with corrosion and leakage are encountered.

PEMFCs usually use hydrogen as fuel. Oxidant supplied to the cell is pure oxygen or air. When the PEMFC uses hydrogen as fuel, the products other than electricity are merely small amount of water and heat, which are harmless to the environment. In addition, since hydrogen can be generated from a variety of indigenous sources, its implementation supports distributed power generation and national energy security.

1.2. Introduction to PEM Fuel Cell

One unit of PEMFC consists of MEA (Membrane-Electrode-Assembly) and supporting components, also known as cell fixture. The MEA is the main part of the cell where electrochemical reaction to produce electricity occurs. The fixture, serving transport as well as providing mechanical support, consists of current collector and flow fields for both anode and cathode of the fuel cell. Figure 1-1 shows schematic diagram of one single cell of PEMFC. Brief description on fuel cell components and their function is given in section 1.2.1.

Figure 1-1 Schematic representation of PEM Fuel Cell (adapted from Birgerrson, 2004)

Hydrogen or fuel in general, flows through flow field channels and diffuses to the anode gas diffusion layer (GDL) while oxidant flows at the cathode side. Gas reactants are distributed through gas diffusion layers taking advantage of porous nature of the GDL material. Then the gas will reach the catalyst layer where three phases –electrocatalyst, electrolyte material, and reactant gases– are in contact to oxidize fuel. By the aid of electrocatalyst, hydrogen will release proton (H^+) and electron (e^-). Mechanism of H_2 electro-oxidation on Pt in acidic electrolyte is hypothesized to proceed by first dissociative adsorption of dihydrogen, which is the *rate-determining step*, followed by electron transfer reaction.

In total, above the reaction can be written as:

The proton (H^+) moves through ion conducting membrane to reach cathode in hydrated form ($H(H_2O)_n^+$, since water molecules are dragged by proton during electro-osmotic process). On the other hand, electron passes through the gas diffusion layer, subsequently the current collector, and then transport through external circuit to generate DC current before it joins proton and oxygen at cathode catalyst layer. In case AC current is required instead of DC current, power conditioner is installed to do the conversion. In the cathode catalyst layer, proton and electron combine with oxygen to produce water through reaction:

The phase of water generated in reaction 1-4 above affects the Open Circuit Voltage of the cell. The theoretical value of OCV for fuel cell operating with H_2 and O_2 at $25^\circ C$, 1 atmosphere is 1.23 Volt when the reaction generates liquid water product. This value decreases to 1.18 Volt when gaseous water is produced instead. The difference between 1.23 Volts and 1.18 Volt represents the latent heat of vaporization of water at standard condition.

Not all of chemical energy contained in reactants is converted into electricity. Some is converted into heat as the reaction is exothermic. Porous electrode helps to remove the heat from the reacting zone. Additional cooler or heater module might be added to cell fixture to enable thermal control of the cell.

Water as product will then leave cathode either by diffusing to cathode GDL along with excessive reactant, evaporation, or back diffusion to anode. Maintaining the balance of water is a challenge in PEM fuel cell since the amount of water in the membrane directly affects its ionic conductivity. Water also plays important role in keeping the activity of Nafion ionomer in interfacial kinetics. It means that sufficient amount of water must exist in the membrane to keep the proton flowing. On the other hand, if too much water exists in the cell especially in cathode backing layer, it will cause flooding that limits oxidant transport into reaction area.

1.2.1. Membrane-Electrode Assembly (MEA)

Similar to other electrochemical system, the PEM fuel cell consists of electrolyte and electrodes (anode and cathode) as the group of components to generate electricity. In

principle, the two electrodes in the cell can be made symmetrically. However, for practical application, cathode often has higher catalyst loading due to lower reaction rate.

1.2.1.1. MEMBRANE

The type of membrane used is cation exchange membrane capable of conducting proton and rejecting electron. The thickness of the membrane is typically in the range of tens to hundreds micrometer. Since the membrane has low gas permeability, this thickness is enough to prevent fuel and oxidant from mixing.

There are a few types of membrane used for PEM fuel cell application but perfluorosulfonic acid (PFSA) membrane is the most common one. It contains polytetrafluoroethylene (PTFE) polymer as backbone, side chain of O-CF₂-CF₂-O-CF₂-CF₂-, and sulphonic acid ion as the active site (shown in Figure 1-2). This site gives path for proton to move from anode to cathode in the presence of water. Nafion® from DuPont is one prominent trademark for membrane used to make MEA in PEMFC. Ionic conductivity is an important PFSA membrane property and is dependent on the level of membrane hydration. This is the reason PEM fuel cell operation is limited to temperature below 100°C. Alternative membranes, e.g. Polybenzimidazole-based membrane, are being developed to enable operation at temperature higher than 100°C (Jalani *et al.*, 2006)

Figure 1-2 (a) Chemical structure of Nafion™ 112, (b) analogous structure for PTFE

1.2.1.2. ELECTRODES

Litster and McLean (2003) defined electrode as components that span from the surface of the membrane to gas channel and current collector. Thus, it includes catalyst and gas diffusion layer. Some factors to consider in choosing electrocatalyst for PEMFC are their reactant diffusivity, high electrical conductivity, good interaction with ionomer, and high level of hydrophobicity (Larminie and Dicks, 2003). Platinum supported by carbon particles is chosen to catalyze reactions at both electrodes since it shows good activity as well as good stability against acidic condition. In the case where CO is present in fuel, other precious metals (usually Ruthenium) are used to avoid Pt poisoning.

Porous gas diffusion layer ensures effective diffusion of reactants and products to and from the catalyst layer. The gas diffusion layer is also an electron conductor connecting the catalyst layer and current collector. GDL also needs to have sufficient heat conductivity since it will conduct the heat of reaction away from the active area. For those purposes, material chosen usually is carbon cloth or carbon paper. Carbon cloth has benefit compared to carbon paper since it has a good porous property even after being hot pressed with membrane to fabricate MEA (Lee *et al.*, 1999). To achieve hydrophobic property, gas diffusion layer is treated with PTFE. Carbon powder is added prior to catalyst ink application to prevent catalyst penetration deep into gas diffusion layer and to increase catalyst utilization efficiency.

1.2.2. Fixture and Bipolar Plate

The cell fixture to support MEA consists of current collector and reactant distributor (flow field). Bipolar plate in principle serves the same function as cell fixture. They are different

in that each face of the fixture is in contact to only one gas diffusion layer, anode or cathode only. On the other hand, the two faces of bipolar plate are in contact with anode of one single cell and cathode of another single cell, which enables it to act as a connector from one cell to the other in stack arrangement. They also function as a separator between cell(s) and the environment. Thus, material chosen must be dense enough so that a small thickness of it will prevent mixing of reactants with ambient gases (air, etc).

Cooling or heating tubes can be mounted within fixture or bipolar material. Therefore, the material is required to have high thermal conductivity. Other requirement is that the material has to be light enough to reduce overall weight of the cell assembly but have enough strength to mechanically support the cell. From supply point of view, inexpensive cost, manufacturability, and availability will also become important criteria. Mehta and Cooper (2003) concluded the above criteria lead to the use of nonporous graphite, coated metal, and composite material for cell fixture or bipolar plate.

1.2.2.1. CURRENT COLLECTOR

The cell is connected through the external circuit via the current collector. Stainless steel or carbon graphite is often used as current collector as they have high electric conductivity required to connect the cell with electrical load. Flow field is often etched on one surface of current collector to reduce material cost while increase contact between current collector and GDL.

1.2.2.2. FLOW FIELD

Flow field topology determines reactant and product transport and distribution through the GDL surface. Current available flow field designs are explained by Li and Sabir (2004), ranging from conventional topology (pin, parallel, etc.) to the modified version (variable cross section, biomimetic, etc.). Material used for flow field must accommodate effective transport of reactant to and product away from reaction site. Hydrophobic material will help to avoid flooding as water is immediately transported outside the cell.

Challenge for PEM Fuel Cell Development

Advancement in cell material and design has led to significant improvement in cell performance since it was used in space flight mission in 1960. Grot (1975) at Du Pont de Nemours and Co. has developed membrane with PTFE backbone to achieve higher stability in the strong oxidative condition, which is later known as Nafion®. Due to innovations in MEA fabrication method, Platinum catalyst loading was successfully reduced compared to the first time solid polymer fuel cell was introduced. This results in lower material cost while at the same time maintaining high power density. On the other hands, developers in fuel cell as well as governmental organizations continue to tackle infrastructure issues (such as hydrogen supply infrastructure) to bring fuel cells closer to public and commercial use.

These facts, nevertheless, does not mean that PEM fuel cell is ready for commercialization. There are still numerous key technical challenges PEMFC have to face before its full potential can be realized. Performance and durability are among the major issues. Higher power density as well as longer lifetime is expected from fuel cell to compete realistically

with other power generating system. The issues in principle are related to the fundamental of cell behavior and performance limitations that occur during operation. On the other hand, complexity in mechanisms and correlation among key parameters in PEMFC as well as its inherent small dimension has presented hurdles in full understanding of fuel cells.

An important part of the development of solution for these challenges is to develop reliable assessment technique capable of identifying cell condition as well as its abnormalities and degradation. It is the intention of current project to contribute in the development of performance limitation identification and analysis for PEMFC.

1.3. Performance Analysis for PEM Fuel Cell

The task of performance analysis includes identification of the key factors beyond cell performance and the use of this information to detect the occurrence of fault. The purpose of this analysis is also to understand the deterioration process over the cell lifetime. Another interest in this area involves transient study to understand the mechanism during swing load (acceleration and deceleration) and start up-shut down in dynamic environment such as automotive environment. This transient study, interesting by itself and important in practical cases, is out of scope of this project.

Different methods and devices are available to carry out the performance evaluation task. The current project deals with electrochemical approaches due to its two important characteristics, in-situ and non-destructive. Two methods of electrochemical testing, Current Measurement Method and Electrochemical Impedance Spectroscopy (EIS), are the focus of this study since both measurements are capable of assessing the performance of a

full fuel cell. Other type of measurement assesses only certain component of the PEMFC, e.g. surface active area. While assuring the performance of individual component fuel cell is crucial, it is difficult to predict the performance of the fuel cell from its component characteristics due to interrelated aspect and interfacial mechanisms occur among these components.

Current Measurement Method, conducted in potentiostatic mode is widely used in galvanic cell testing. This testing is relatively straightforward in terms of implementation and result analysis. Polarization curve, as the product of this measurement, has been widely used to indicate performance limitations in certain region of fuel cell operating potential.

EIS involves the application of a small perturbing signal to the system to obtain information about cell impedance response. This relatively new method requires additional modules, like ac signal generator and frequency response analyzer, as well as certain techniques to interpret the measurement result. However, this method is powerful in giving information of mechanisms occurred at the bulk as well as at interface between elements of the fuel cell.

In addition, segmented fuel cell and thin film agglomerate model were incorporated into the available measurement methods. Both approaches are expected to enhance the capability those methods mentioned previously in identifying and analyzing key factors affecting the cell performance. Segmented fuel cell is a specifically designed fixture to facilitate spatially resolved in-situ measurement. Development of this fixture was driven by the desire to understand the working parameters distribution over the geometric area of the

cell. It is known that the uneven load distribution can decrease the current generation when one or more segments limiting the performance of other parts of the cell. In addition, the inhomogeneous extent of mechanisms can lead to cell degradation.

According to the Thin Film–Agglomerate model, the electrodes of PEMFC can be divided into two regions. In the first region, agglomerate region, catalysts whose pores contain active reaction site form clusters and Nafion electrolyte filled these pores. A thin layer of the same electrolyte covering this agglomerate region builds the second, thin film region. This structured description of electrode regions provides theoretical basis in understanding mechanisms occurring at the main site for electrochemical reaction, especially the diffusion-related ones. Diagnostic equation derived from this model uses data obtained from current measurement method and EIS to reveal the performance limiting factors, which are difficult to capture by using these two basic methods. Further explanation of this model as well as the segmented fuel cell is presented in Chapter 3.

One challenging issue in the analysis of PEMFC is water related processes affecting the cell performance due to complex dependence of cell output on its moisture level. Complex balance needs to be maintained to ensure sufficient amount of water for cell operation while preventing too much of it to avoid flooding that reduces performance significantly. At the operating temperature range of PEMFC (below 100°C), water exists in both water and gaseous forms. Within the cell, water flows from one electrode side to the other caused by certain mechanisms (e.g. Oxygen Reduction Reaction creates concentration difference for water to diffuse away from cathode) while at the same time affecting other mechanisms, (e.g. proton conduction). Considering the important effect of water-related mechanisms on

the extent of electron generation rate, one part of this project is dedicated to further study the capability of both current measurement method and EIS to identify this type of processes. Current and impedance change were captured during experiment period while certain scheme affecting the MEA components humidity was applied to the cell.

1.4. Objective and Scope of Research

The research focuses on the application and improvement of the Current Measurement Method and Electrochemical Impedance Spectroscopy in order to identify and analyze key factors affecting the performance of PEM Fuel Cell. In order to achieve its objective, the scope of this work includes:

- ⊕ Implementing the application of current measurement method and EIS to the segmented fuel cell. Included in this work is the investigation of the effect of flow field design and operating potential to performance magnitude and spatial variation of cell performance.
- ⊕ Implementing the thin film-agglomerate model as an approach to identify and isolate the cause of performance losses in oxygen and air PEM fuel cell.
- ⊕ Observing the responses of the cell as well as identifying the key factors affecting its performance as humidification and back pressure schemes influencing the moisture content of the cell are applied to the system.

Fuel Cell and Assessment Approaches

Although from thermodynamic point of view fuel cell has higher efficiency compared to most energy converting device, limitations of processes occur in fuel cell do not allow actual fuel cell to reach high ideal efficiency. This chapter explains the root causes and mechanisms that result in fuel cell performance degradation. Operating aspects of the fuel cell, (including distinct kinetic and thermodynamic aspects) are described in the first part. Later parts of this chapter discuss two electrochemical methods functioning as evaluation approaches to isolate the cause of cell performance degradation.

2.1. Operating Aspects of PEMFC

2.1.1. Open Circuit Voltage

Open Circuit Voltage (E) for fuel cell running on hydrogen and oxygen is obtained from Nernst equation

$$E = E^o + \frac{RT}{nF} \ln \frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \quad \text{while} \quad E^o = \frac{-\Delta G^o}{nF} \quad [2-1]$$

which yields 1.229 V for PEM fuel cell operating at Standard Temperature Pressure with liquid water as the product or 1.18 Volts when water product is in gaseous form. In above equation, E^o is standard electrode potential, R is ideal gas constant (8.314 J/mol.K), T is absolute temperature, n is the mole of the reactants involved, F is the Faradaic constant, and P_i is the partial pressure of species involved in the reaction. The difference between 1.229 volts and 1.18 volts represents the latent heat of vaporization of water at standard conditions (Hooger *et al.*, 2003). At practical operating condition, this OCV value varies between 0.9 to 1 Volt dependent on the fuel and oxidant used, impurities, and temperature.

In addition to lowering the reactant's partial pressure, it is possible that the impurities react at electrode (usually anode) causing mixed potential.

Ideally, this equilibrium potential can remain the same independent of the electrical current drawn. In reality, there are irreversible processes that cause losses and decrease in potential as the cell operates (Visnyakov, 2006). In the section below, phenomena found in PEMFC and typical losses related to them are discussed.

2.1.2. Fuel Crossover and Internal Current

Due to its small molecular size, small amount of hydrogen is able to diffuse through membrane without first being protonized and directly react with oxygen at cathode in particular when the membrane has become dry. To lesser extent, electrons can also pass through the membrane causing internal current. For each hydrogen molecule, two electrons are lost and not contributing to the cell's electrical work via external wiring. For low temperature fuel cell, this loss significantly decreases the value of open circuit voltage (OCV). It is shown that fuel crossover equivalent to 1 mA/cm^2 can decrease OCV to 0.97 Volt (Larminie and Dicks, 2003). Fuel crossover can be avoided by increasing the thickness of the membrane but trade off transport properties of membrane must be considered.

2.1.3. Electrode Reaction and Activation Overpotential (η_{act})

Even though the overall reaction for PEMFC (see equation 1.4) is thermodynamically viable, as suggested by positive Gibbs energy value, the reaction kinetic of the cell dictates that the current generation will not happen until certain energy barrier is overcome. This

energy barrier can be reduced by addition of catalyst that provides alternative pathway with lower energy level for the reaction. Figure 2-1 shows the illustration of activation barrier for charge transfer reaction at anode between metal (Pt electrode) and chemical species (Hydrogen). $\Delta G1$ is the original activation energy of the reaction which can be lowered to $\Delta G1'$ with the presence of catalyst (Fisher, 1996). In PEMFC, platinum is *catalytic electrode* which acts as electrode that supplies electrons to the chemical species when the charge transfer reactions occur and works as catalyst at the same time due to its high activity for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR).

Figure 2-1 Illustration of activation energy for anode charge transfer reaction (adapted from Fischer, 1996)

Even though platinum has been very effective in reducing the activation energy, there are still portion of the barrier left for the reactions to occur ($\Delta G1'$). A portion of the cell potential known as activation overpotential or activation loss is required to overcome this kinetic barrier. In general, the relationship between activation loss and current production resulted from the reactions is described by Butler-Volmer equation:

$$i = i_o \left[\frac{C_R^*}{C_R^{0*}} \exp\left(\frac{\alpha n F \eta}{RT}\right) - \frac{C_P^*}{C_P^{0*}} \exp\left(\frac{-(1-\alpha) n F \eta}{RT}\right) \right] \quad [2-2]$$

where

i is the current density generated at the expense of η overpotential,

i_o is the exchange current density, which represent equilibrium current at OCV

C_R^* and C_P^* are the actual surface concentration of product and reactant,

C_R^{0*} and C_P^{0*} are the reference concentration of product and reactant,

α is known as transfer coefficient, depends on expresses the symmetry of activation barrier.

n is the number of electron involved in the reaction.

In other words, the Butler-Volmer expression states that current increases exponentially with activation overpotential, which is one of the reasons why the cell is considered to

behave nonlinearly. At low overpotential, Taylor expansion ($e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$) can be used to

approach this equation 2-2:

$$i = i_o \left\{ \left[1 + \frac{cnF\eta_{act}}{RT} + \frac{1}{2!} \left(\frac{cnF\eta_{act}}{RT} \right)^2 + \dots \right] - \left[1 - \left(\frac{(1-\alpha)nF\eta_{act}}{RT} \right) + \frac{1}{2!} \left(\frac{(1-\alpha)nF\eta_{act}}{RT} \right)^2 - \dots \right] \right\} \quad [2-3]$$

By neglecting the terms with order higher than one and rearrangement, equation 2-3 now becomes:

$$\eta_{act} = \frac{RT}{nFi_o} i \quad [2-4]$$

High overpotential condition corresponding to irreversible reaction process where forward direction dominates, results in cancellation of the second part of the exponential term.

Since the operating condition of interest in fuel cell is in the area where the overpotential is considerably high (more than 100mV), this simplification is proved to be useful for most cases. In this case, Butler-Volmer equation can be rewritten as:

$$\eta = -\left(\frac{RT}{\alpha nF}\right) \ln i_o + \left(\frac{RT}{\alpha nF}\right) \ln i \quad [2-5]$$

Plotting $\eta_{act,c}$ as a function of $\ln i$ will give linear line:

$y = a + b \ln i$ where $a = - (RT/\alpha nF) \ln i_{o,c}$ and $b = RT/\alpha nF$.

The plot is widely known as Tafel plot and b as Tafel slope. By fitting experimental data to equation 2-4, exchange current density can be obtained by extrapolating the line (that is at $\eta_{act,c} = 0$) and calculation on b value can give transfer coefficient α .

Different reactions mechanisms occur at fuel cell electrodes. HOR, which consists of adsorption of hydrogen molecule onto the surface of catalyst followed by the release of proton and electron, is relatively simple and fast compared to the ORR counterpart. Cathode reaction involves more species and complicated steps resulting in far more sluggish reaction reflected by its low exchange current density. For reactions catalyzed by platinum in acidic condition, $i_{o,HOR}$ is approximately 10^6 times higher than $i_{o,ORR}$ (Constamagna and Srinivasan, 2001a). Slower reaction also means higher overpotential is required to surpass the activation barrier. This is the reason why loss in cathode makes up the biggest part of the losses in PEM Fuel Cell.

The differences in reaction mechanisms also leads to different expressions for the two reactions, stemmed from simplification of Butler-Volmer equation above. Reaction at anode side is better expressed by equation 2-4 where low overpotential is required to drive reaction. On the contrary, cathode behavior is well explained by Tafel equation (equation 2-5).

Activation loss is closely related to kinetic performance of the cell. Therefore, the effort to reduce the activation loss is a matter of improving kinetics of electrochemical reactions. Butler-Volmer equation (2-2) is used as guideline to improve current generation (i). Recalling equation 2-2,

$$i = i_o \left[\frac{C_R^*}{C_R^{0*}} \exp\left(\frac{\alpha n F \eta}{RT}\right) - \frac{C_P^*}{C_P^{0*}} \exp\left(\frac{-(1-\alpha) n F \eta}{RT}\right) \right]$$

It can be seen that the rate of each electrode reaction increases with the reactant concentration (C_R^* , which for gaseous system is the gas partial pressure), catalyst properties (α and η), and decreases with temperature. As the result, increase in system total pressure will increase reactants partial pressure and push the reaction toward products in each electrode (proton at anode and water at cathode). Choice of operating temperature has more complicated consequence as increase in temperature will lead to faster reaction rate but there is water evaporation issue which is difficult to analyze.

The search for electrocatalyst having energy barrier (η) lower than that of platinum in PEMFC operating condition seems to give very few options. Other approaches can be explored for higher exchange current density in order to accelerate electrode reaction. It is known that i_o depends highly on surface active area. Higher catalyst loading yields in larger area available for reaction due to higher amount of catalyst particles, which in turn will increase exchange current density. Increase in porosity, which means more available catalyst active site, will also improve the cell performance. Care must be taken in MEA fabrication so that the higher catalyst loading will not present hindrance for mass transport.

2.1.4. Charged Material Transport and Ohmic Overpotential (η_{ohm})

Also known as resistance losses, ohmic overpotential is a composite of the general electronic and ionic resistances through fuel cell. The characteristic of this loss is that the overpotential increases linearly with the increase of current density. That is to say that resistance (r) is essentially constant, not a function of current density (Weber and Newman, 2004). This allows Ohm's law to be used to express this polarization:

$$\eta = ir, \eta [=] \text{ Volt} \quad [2-6]$$

with r (resistance) consisting of electronic and ionic resistance. The electronic resistance comes from the gas diffusion layer (GDL), current collector, catalyst, and contact resistance between the components of the cell. Ionic resistance mainly comes from the resistance to proton movement across the membrane.

The magnitudes of these ionic and electronic resistances are different due to the differences in mechanism and structure in charge transport, as illustrated in Figure 2-2. Free electron model for the behavior of valence electron in metal structure can be used to describe the electron transport within those electron-conducting materials. This model assumes that valence electrons are completely detached from the metal atom lattice. Therefore, they are free to move in respond to applied potential field around the immobile atoms and limited only by the scattering from the lattice.

The transport of proton mainly depends on hopping mechanism from one charge cluster to the other cluster. This cluster, in PEM, is provided by the end of side chain, the sulphonic acid functional group. Certain fraction of free volume is required to facilitate ion transport. The movement of the ion is highly assisted by the movement of water as it flows through

this free volume. Therefore, water content of the membrane plays an important part in proton conductivity.

Figure 2-2 Illustration charged species across their respective conductor (O'Hayre *et al.*, 2006)

Another factor differentiating proton and electron conductivity is their concentrations as charge carriers. The abundance of electrons within electronic conductor results in high charge carrier concentration. Along with its transport mechanism explained above, high electronic conductivity (around $10^6 - 10^8 \Omega^{-1} \cdot \text{m}^{-1}$) can be achieved. On the other hand, ionic conductivity for polymer electrolyte is only around $10^{-4} - 10^{-2} \Omega^{-1} \cdot \text{m}^{-1}$ (O'Hayre *et al.*, 2006).

Some approaches to suppress this loss are to apply higher temperature, to use more conductive and thinner material to carry charges (electrolyte, electrode, and current collector), and to reduce the contact losses (Mehta and Cooper, 2002).

2.1.5. Mass Transport and Concentration Overpotential (η_{conc})

The rate of electron generation from fuel through electrochemical reaction (generally known as current) is a function of flux of reactants (N) reaching the electrode surface. The correlation between current and the flux is given by the equation below:

$$i = nFN \quad [2-7]$$

which accounts for three processes of reactant transport, i.e. migration, convection, and diffusion.

Migration is defined as the transport of charged species at the interfacial region of electrode/solution caused by electrical field between them.

$$N_i^{\text{migr}} = -z_i u_i F c_i \nabla \Phi \quad [2-8]$$

Migration does not present significant problems in most operation of PEM Fuel Cell. This is because the electrolyte polymer itself has an abundance of sulphonic acid ions which, in the presence of water, is capable of maintaining the potential difference at the interface of the electrode even without the addition of excess non-electroactive ions (supporting electrolyte).

Convection occurs when natural or induced mechanical force is applied to a fluid stream.

The flux of molecule caused by the act of convection is expressed by:

$$N_i^{\text{conv}} = c_i \bar{v} \quad [2-9]$$

with c = concentration of the species and v = bulk velocity of the reactant.

In fuel cell, convection takes place in flow field where reactants are transported to and products are moved out from gas diffusion layer (GDL). Flow field is also responsible to

maintain even reactant distribution over the surface of GDL. This task is challenging and therefore various flow field designs, some of which are shown in Figure 2-3, have been analyzed for their transport capability. Study on convection transport in fuel cell showed that length of the path, rib to channel width ratio, and the cross section area have to be considered for achieving optimal reactant and product transport.

Figure 2-3 Several Flow Field Topology Designs

Diffusion occurs as the consequence of concentration gradient between catalyst layer and flow field. The electrochemical reaction causes reduction of reactants concentration due to species depletion. At the same time, the reaction product is accumulated at the three-phase boundary. The flux for gas i (following ideal gas law), due to diffusion, is given by

$$N_i^{diff} = -\frac{D_i}{RT} \nabla p_i \quad [2-10]$$

The porous nature of GDL and catalyst layer allows two types of diffusion to occur. Fickian diffusion occurs when mean free path of the molecule is relatively short compared

to the pore size. Knudsen diffusion on the other hand occurs when the mean free path is relatively long compared to the pore size causing the molecule to collide frequently with the pore wall (Geankoplis, 1983). Other than in GDL, this diffusion is important for molecule transport through very small pores in the catalyst layer.

Concentration overpotential arises from mass transfer limitations due to insufficient supply of reactants to the catalyst layer. This condition usually occurs at high current density where the rate of depletion through reaction is faster than the speed at which the reactants may be replenished by diffusion from bulk gases to the interfacial region. In most case, the insufficient supply is due to the presence of hindrance for reactants to reach catalyst layer or ineffective product removal. As the consequence, the current will not increase even with additional overpotential.

In PEMFC, accumulation of water product in the cathode is the prominent part of concentration limitation. Figure 2-4 indicates the water balance at the cathode catalyst layer. Water supply (red) to this layer is due to water vapor supply from oxidant stream (vapor stream), electro-osmotic drag by proton as it travels through membrane and water generation as the result of reaction. On the other hand, water removal (blue) is facilitated by back diffusion from cathode to anode due to difference in water partial pressure, capillary transport, and evaporation of liquid water away from the catalyst layer (He, 2003).

Figure 2-4 Water balance at cathode catalyst layer and the cell in general

Water accumulation occurs when its removal rate is slower compared to the supply rate and it blocks the path for oxygen to reach catalyst layer. As the result, oxygen concentration becomes zero at the catalyst layer and limiting current density (i_{lim}) is reached.

$$i_L = nFD_{eff} \frac{C_R^0}{\delta} \quad [2-11]$$

As mass transport is related closely with concentration of reactant at the catalyst layer, it will affect the cell potential (from equation 2-1, Nernst equation) and rate of reaction (Equation 2-2, Butler-Volmer equation). Derivation of these equations will lead to:

$$\eta_{conc} = c \ln \frac{i_L}{i_L - i} \quad [2-12]$$

$$c = \frac{RT}{nF} \left(1 + \frac{1}{\alpha} \right) \quad [2-13]$$

However, the calculated c is often significantly higher than the predicted value obtained from equation 2-13. Empirical equation below is often used to express concentration overpotential (Constamagna and Srinivasan, 2001b):

$$\eta_{conc} = k \exp(ni) \quad [2-14]$$

The use of PTFE, a hydrophobic substance, in electrodes can effectively suppress flooding by assisting water removal from cathode catalyst layers. Mass transport overpotential can also be minimized by using higher pressure to increase partial pressure of reactant and improve design of fuel cell to promote better transport.

2.2. Electrochemical Testing to Evaluate the Performance of PEMFC: Current Measurement & EIS

Different methods have been developed to evaluate fuel cell performance and to understand the mechanism behind its degradation. Hinds (2004) categorized methods to evaluate PEM fuel cell into three kinds of physical experiment (structural, chemical, and electrochemical testing) and modeling. In addition to those categories, the novel imaging method, e.g. neutron tomography conducted by Satija *et al.* (2003), is a powerful method to observe temperature and water related mechanisms. However, this method is not cost effective and only few research institutions as well as national laboratories own the device.

Mathematical model has been a great tool to accelerate understanding in PEMFC and its rapid advancement enables 3D and two phases water flow simulation at present time. However, physical experiment is absolutely required to serve at least two purposes: to validate knowledge obtained from modeling and to evaluate the behavior of operating fuel cell so that any deterioration in performance can be detected earlier.

The physical testing methods focus on different aspects. Structural testing, an example of which is Scanning Electron Microscopy, provides morphological identification to observe components structure especially catalyst layer and GDL. Chemical testing deals with material stability. One example for this is observation of membrane degradation rate by analyzing fluoride ion in cathode effluent. Material and component degradation, as probed by structural and chemical testing, are important aspects in fuel cell operation as not only they reduce the cell reversible potential, but also reduce the lifetime of the cell. Due to their destructive characteristic, structural and chemical testing are often used for post mortem analysis conducted in ex-situ environment.

Electrochemical testing, being the in-situ measurement for fuel cell, complements other physical measurement to identify the performance of fuel cell as an operating unit. This is because it is difficult to predict the performance of the operating cell only from the characteristic of its individual components. There are contact resistances and property distribution differences during assembly process in addition to interfacial mechanism. In this testing, cell parameter is obtained by exploiting the potential-current correlation. Nondestructive nature of this test also enables one to perform durability test over certain range of time. Current Measurement Method and Electrochemical Impedance Spectroscopy (EIS), which belong to this type of measurement, were chosen for this project.

2.2.1. Current Measurement Method and Polarization Curve

Current measurement method registers current generated under certain cell potential. As a convention, current density is used to state cell performance instead of merely current since the current generated by fuel cell increases with surface area. The current density is affected by many essential factors such as operating condition, design, and material of the cell, and reactants being used. Therefore, high current density is an indication of optimum synergy among these factors.

If the OCV value is known, the amount overpotential required to overcome the losses for current to flow under this potential can be obtained. Further, if the current density is evaluated for full cell potential range (OCV or low overpotential to the point where limiting current density is reached), polarization curve showing the relationship between cell potential and current density can be drawn. This mode of measurement is known as

potentiostatic mode (potential control). Polarization curve can also be done under galvanostatic (current control) by measuring cell potential under certain current.

Polarization curve is widely used in fuel cell study to identify the cause of losses reflecting the characteristic of the cell under observation. This identification is based on the identification of losses in section 2.1

$$E_{actual} = E_{rev} - \eta_{act,a} - \eta_{act,c} - \eta_{ohmic} - \eta_{conc} \quad [2-15]$$

$$E_{actual} = E_{rev} - \frac{RT}{nFi_{o,a}} i - (a + b \ln i) - ir - c \ln \frac{j_L}{j_L - j} \quad [2-16]$$

Typical polarization curve shown in Figure 2-5 shows the three regions of fuel cell operation. Each type of overpotential dominates one region. By fitting the experimental data to the model in equation 2-16, operating cell characteristics such as exchange current density, cell resistance can be obtained. In addition, comparison among different cell performances as the result of running the fuel cell at different operating conditions can be made. The better the cell performance is, the closer the polarization curve to the theoretical voltage will be. In other words, a better cell will give higher current density at certain cell potential and vice versa.

Williams *et al.* (2005) made careful analysis on the polarization curve to extract information of several sources polarization of fuel cell, namely non-electrode ohmic, electrode ohmic, non-electrode concentration, electrode concentration, activation losses from Tafel slope, and activation losses from catalyst activity. Here they assumed first order oxygen reaction reduction as the basis for their analysis. The strength of this analysis is its

capability to isolate different kind of losses based on theoretical assumptions. On the other hand, the isolation process consisted of several sequential and dependent steps where erroneous analysis in one step will affect the accuracy of analysis of other parts. Some iteration is also required to identify electrode ohmic resistance and non-electrode concentration resistance.

Figure 2-5 Cell voltage-current density characteristic curve (Polarization Curve) of PEM Fuel Cell

To obtain polarization curve, large perturbation signal needs to be applied to the cell. For ramp test, the scan range can be from open circuit to around 0 V vs. reference or on the other direction. The step between 100 mV – 300 mV is common to conduct step test. As the consequence, the condition of the cell alters especially the moisture content and the transport it affects. In some experiment, current was measured in certain point instead of total registration (to acquire polarization curve) to avoid change in cell condition. Section 2.2.2 below explains Electrochemical Impedance Spectroscopy (EIS), a powerful method to identify mechanisms occur within fuel cell which work based on the principle of small perturbation signal.

2.2.2. Electrochemical Impedance Spectroscopy

2.2.2.1. OVERVIEW ON EIS FUNDAMENTAL AND ITS DEVELOPMENT IN PEM FUEL CELL

There are different fundamental microscopic processes occurring within cell materials as well as at interfaces among them when potential difference is applied across those materials. Unique polarization pattern occurs, including charge transfer at the electrode-electrolyte interface as well as charged and uncharged material transport through the conductors. When the applied potential is reversed (or perturbed), each polarized region will change based on their characteristic rate (Barsoukov and McDonald, 2005). This allows identification of different processes through response observation when particular perturbation capable of reversing the applied potential is introduced to the system. This is the basic principle behind the EIS registration.

EIS uses transient and small amplitude signal to perturb the system of interest. Perturbation is applied in a broad frequency range to obtain full characteristics of the system. This differentiates EIS from current measurement method which relies on steady, large amplitude perturbation that will drive the system far from equilibrium (Bard and Faulkner, 2001). Electrochemical system is a complicated system due to electrochemical reaction taking place in the electrode-electrolyte and mass transport within bulk and across the interface. There are also chemical and electrical equilibrium to be maintained at the same time. This interrelation leads to a non-linear nature of the electrochemical cell. As a consequence, large perturbation may lead to nonlinear response of the system.

Impedance in principle is a transfer function stating the ratio between the response and perturbation signal given to the system in frequency domain. It is important to note that, as

shown in explanation below, impedance is calculated instead of measured. As the impedance method is derived from classical transfer function, linearization must be done to the system. The solution is based on the local application of the linear system theory, which allows the approximation of the non-linear system with the linear term if the equivalent linear equations are known at every point of its steady state non-linear characteristic. This approximation requires that only small amplitude of perturbation is used, which is the character of EIS mentioned previously. For PEM Fuel Cell with OCV at 25°C is around 1.23V, the signal should be lower than terminal potential $v_T = RT / F = kT / e \cong 25\text{mV}$ at 25°C. Applying perturbation of higher magnitude than this value will cause non-linearity which result in inaccurate measurement. It is worth noting that the mean potential of the working electrode (dc part) serves to set steady state (equilibrium) for EIS measurement determined by ratio of oxidized and reduced forms at electrode-electrolyte interface.

From the theoretical point of view, any kind of signal including step or Dirac impulse can be used for EIS measurement. However, sinusoidal (alternating) wave is considered the most practical for conducting EIS (Gabrielli, 1998). The reason lies in the ease of obtaining the transfer function. If we applied small alternating (ac) sinusoidal signal, which is the case in this research:

$$E_t = E_o \sin(2\pi ft) \quad [2-17]$$

the response of the system, current at phase shift ϕ , can be registered.

$$I_t = I_o \sin(2\pi ft + \phi) \quad [2-18]$$

We can otherwise applied current to the system and measure the potential of the system. Impedance is calculated as:

$$Z_t = \frac{E_t}{I_t} = Z_0 \frac{\sin(2\pi ft)}{\sin(2\pi ft + \varphi)} \quad [2-19]$$

which is analogous to Ohm's Law. It is more common to write impedance in the form of complex number obtained by Fourier-transforming the equation and applying Euler expression. As $\omega = 2\pi f$,

$$Z(\omega) = Z_0 \exp(j\varphi) = Z_0 (\cos \varphi + j \sin \varphi) \quad [2-20]$$

We can see from equation 2-20 that the impedance is a function of frequency and independent of time. In practice, signal is generally applied and analyzed in frequency domain instead of time domain to avoid the Fourier analysis which can be computationally difficult and time consuming. The algorithm for Fourier analysis is also difficult to implement for frequency below 10 Hz. Figure 2-6 showed the schematic diagram of Frequency Response Analyzer module to carry out EIS in this project. Signal generator generates perturbation signal and applies it to the system. The response of the system is compared to two synchronous references signal, one in phase while the other 90° out phase with the perturbation signal in order to calculate the Real and Imaginary part of impedance.

Figure 2-6 Schematic Diagram of Frequency Response Analyzer – FRA (Gabrieli, 1998)

2.2.2.2. DATA PRESENTATION AND ANALYSIS USING EQUIVALENT CIRCUIT APPROACH

The impedance data of the system under observation is commonly presented in the form of Nyquist diagram, plotting real component of impedance on x-axis while the imaginary part on y-axis (for fuel cell it is common to plot the *negative* value of imaginary part alternatively). The Bode diagram is sometimes used instead of Nyquist diagram as it can reveal the dependence of both magnitude and phase on frequency. Bode and Nyquist diagram are shown in Figure 2-7 (a) and (b). As impedance is an information property of the object rather than a physical reality, model approach is needed in interpreting the result to understand process within the object under study.

Figure 2-7 (a) Nyquist diagram, (b) Bode diagram, and (c) the equivalent circuit of system with two time constants

Equivalent circuit (Figure 2-7 (c)) or also known as structural model is often used to interpret the impedance response. This approach uses electrical elements as analog to reproduce the properties of the electrochemical cell (MacDonald, 2006). The elements are connected from one to another according to certain relationship describing the nature of system. The advantage of this approach is its simplicity and reduced number of parameter

while capable of capturing system parameter (Vladikova, 2004). Besides structural modeling, classical modeling which extracts system parameters through theoretical derivation of a set of integral-differential equations is also used in lesser extent. Only the first approach will be discussed further.

Below are several common equivalent circuit elements used to analyze PEM fuel cell:

1. Resistor (R)

This element describes the resistance to current flow or charged material transport. High Frequency Resistance (HFR) and Charge Transfer Resistance (R_{ct}) are used to explain impedance spectra of the system. HFR can readily be obtained from Nyquist diagram above as the intercept of the curve with real component of impedance axis. This resistance covers the mechanisms related ohmic limitation, which was explained in section 2.1.5. In general, the membrane (electrolyte) makes up the largest portion for this resistance so that this loss is often referred exclusively to membrane resistance. The charge transfer is the resistance for the Faradaic reaction at the interface of electrode-electrolyte.

$$\frac{1}{R_{ct}} = \left(\frac{\partial i_F}{\partial E} \right)_{c_i}$$

In Nyquist diagram, the diameter of the high frequency arc is the summation of HFR and the R_{ct} .

2. Capacitor (C)

In general, this element represents phenomena when a thin layer of non-conducting material separates two conducting surfaces of same amount of charge but opposite polarities capable of storing/restoring energy in the presence of electrical field. In

PEMFC, the electrode-electrolyte interface resembles this phenomenon. Electrode can only transport electron and inhibit proton movement. PEM or electrolyte works the other direction. As the result, electron line up at this fact prevents charges to move across the boundary and therefore very thin separation layer at membrane-electrode interface was formed (the double layer capacitance).

3. Inductor (*L*)

This element is mostly attributed to the inductance of measurement device when it appears at the highest frequency range. On the other hand, inductance loop occurs at low frequency is attributed to adsorption of gas into the catalyst surface. However, Sadkowski (2005) argued that negative capacitor should be assigned to represent the adsorption process since in general inductor is element capable of storing/restoring energy in the presence of magnetic field.

4. Warburg Impedance (*W*)

The derivation of Warburg Impedance back to 1899 for diffusion process enables the implementation of (electrical) impedance concept into electrochemical system. Care must be taken for its application only for semi-infinite diffusion to a planar surface. Warburg assumed the concentration of electroactive species to be zero at electrode surface stating complete mass transport control (MacDonald, 2006). When the diffusion occurs at finite/non quiescent condition, which is often the case for PEMFC, Nernstian diffusion should be used instead.

5. Constant Phase Element (*CPE*)

While the capacitance of ideal capacitor is independent of frequency, study on double layer at the solid electrodes usually showed deviation of this characteristic. This deviation correlates with surface roughness, degree of polycrystallinity, and the

presence of absorbable anion at the surface of electrode. Constant Phase Element is meant to take into account this diffusion. Examination on formula for CPE impedance value given in Table 2-1 showed that formula is generalization of other impedances.

The first three components (R, L, and C), adapted from electrical impedance concept, are lumped components describing homogeneous systems and are not affected by frequency applied. The properties of Warburg parameter and Constant Phase Element, which are derived only for electrochemical system, are affected by measurement frequency. Table 2-1 lists the formula for impedance of elements above while the response of individual element in Nyquist diagram is given in Appendix B.

Table 2-1 Equivalent circuit elements for EIS data interpretation

<u>Element</u>	<u>Symbol</u>	<u>Impedance</u>
Resistor	R	R
Capacitance	C	$-\frac{i}{\omega C}$
Inductance	L	$i\omega L$
Warburg	W	$\sigma(i\omega)^{-1/2}$
Constant Phase Element	CPE	$T^1(i\omega)^{-n}$

Note:

$$i = \sqrt{-1}$$

$$\sigma = \frac{(\partial I / \partial C_o)_{E, C_R}}{nFAD_o^{1/2} 2^{1/2} (\partial I / \partial E)_{C_o, C_R}} + \frac{(\partial I / \partial C_R)_{E, C_o}}{nFAD_o^{1/2} 2^{1/2} (\partial I / \partial E)_{C_o, C_R}}$$

The weak point of equivalent circuit (analog) approach is a set of data can be represented by different equivalent circuits with equal statistical match (usually using Chi square analysis). In other words, the representation of the electrochemical system is not unique. More experiments and knowledge about fundamental physics behind the dataset are required to select which fitting is the best.

2.2.2.3. ESTABLISHED EIS MODEL TO STUDY PEM FUEL CELL

There are numerous equivalent circuits for electrochemical systems due to various possible mechanisms occur within them. In most electrochemical system, EIS is used to unveil adsorption, detection of radicals, diffusion control mechanism, et cetera. The circuit models range from one to three impedance arcs/loci for PEM Fuel Cell, the forms of which differ one to another, depending on the nature of MEA and operating condition. Therefore, it is relatively difficult to conclude particular equivalent circuits to model broad range of PEMFC. Nevertheless, some models are widely known and they set framework for the development of later models. This section discusses these pioneering models and their relevance with PEM Fuel Cell. Most modeling covers specific aspect of the system under interest. Fuel cell is no different. As explained further, models below put their focus in certain part of the cell, e.g. interfaces, microscopic or electrode, and catalyst zone.

Randles Model

Figure 2-8 shows the electrolyte-electrode domain described by Randles model. Equivalent circuit representing this electrode-electrolyte interface domain was built by four related elements. The parallel elements (C_{dl} and $Z_w + R_{ct}$) represent the sum of Faradaic current, i_F (from charge transfer reaction) and i_C (from double layer charging) which is the basic assumption in most models. In reality, these two kinds of current are inseparable but treatment to do so is tedious and successful approach has not been established.

Electrolyte resistance (R_s) element was included in the circuit in series since all currents must pass through this resistance. R_s and Z_w are not affected by electrochemical reaction occurring at the surface of electrode since they represent bulk properties (R_s represent bulk

resistance and Z_w represents diffusion feature of reactant/species toward electrodes). On the other hand, C_{dl} and R_{ct} depend on dielectric and insulating features at the electrode/electrolyte interface which is affected by the electrochemical reaction (Katz, 2003).

Figure 2-8 (a) Illustration of domain for Randles model (Moon and Sook, 2003), (b) equivalent circuit (c) System impedance response according to Randles model

Randles model is among the first and widely known model to represent electrode with fast reaction kinetics. This model is suitable for liquid electrolyte system but some adjustments need to be made for PEM Fuel Cell and solid-solid system. As mentioned previously, finite diffusion should replace the Warburg impedance while surface roughness requires CPE to replace capacitor. In addition, solid material can consist of different crystalline structures whose interface will polarize uniquely when the material is subjected to alternating applied potential. As the result, the impedance response from different MEA will give different spectra. However, this model has made a comparative base for the development of equivalent circuit for solid-solid system.

Polarisable Electrode Model

With the absence of Warburg element, the Randles model turns into Polarizable Electrode model as shown Figure 2-9 (a) and (b). The equivalent circuit now consists of electrolyte resistance, double layer capacitance, and charge transfer resistance. In general, one perfect semicircular in Nyquist diagram can be attributed to resistor and capacitance in parallel arrangement having time constant $\tau = RC$.

This model corresponds to condition when charge transfer resistance is large enough to mask the mass transfer (performance is under kinetics control). Similar with the previous Randles model, the domain of current model is electrode-electrolyte interface. This circuit also follows the same basic working assumption, that is, the current flow is the addition of the current of double layer charging and of surface reaction.

Figure 2-9 Polarizable Electrode Model (a) Equivalent Circuit (b) Nyquist Diagram

Polarisable electrode model can be used to represent PEM Fuel Cell when anode impedance is ignored due to small losses at small and medium current density. However, it has been reported that under high load condition, increase of activation polarization at

anode side can cause additional arc of in cell response (Ciureanu, 1999). Depending on the electrode material used, capacitance double layer may be changed with CPE.

Transmission Model

Transmission model of uniform pore, introduced by de Levie (1967), suggests that interface impedance due to charging of the double layer capacitance is distributed along the length of a uniform pore. Surface reaction was not accounted in the model. Nevertheless, modification to account for Faradaic reaction can be done to allow the flow of steady-state current (Raistrick, 1990). As shown in Figure 2-10, the impedance is modeled by network of resistance and capacitance, similar to ladder structure. If the distribution effects are negligible and the current penetration is complete through the electrode, this transmission model will actually turn into polarisable electrode model (Springer and Raistrick, 1989). Porous electrode behavior, for example GDL of fuel cell, can be approximated using this model.

Figure 2-10 Equivalent Circuit for Transmission Line Model to describe uniform pore at electrode surfaces

Thin-film/agglomerate model

Proposed by Raistrick and Springer (1989), this model was said to give complete treatment for fuel cell performance as it considers electrochemical reaction and diffusion of gasses through the porous electrodes. According to this model, gas has to diffuse through thin layer film covering the agglomerate area and electrolyte filling the pore of catalyst before

reacting at the catalyst surface. Therefore, the response of the PEM Fuel Cell should consist of three arcs. The first arc reveals the interface reaction, the second arc describes the diffusion at agglomerate region, while the last shows the dynamic of thin layer region.

What made this model exceptional is the availability of mathematical description of the model. In other words, their equivalent circuit model was obtained from mathematical approach and in addition, experimental works have been done to support the model. Part of the work in this project includes the incorporation of this thin agglomerate model to separate different sources of performance loss for $H_2 - O_2$ /air fuel cell. Detailed explanation about this model is given in Chapter 3.

Segmented Fuel Cell and Thin Film - Agglomerate Model

Two approaches introduced to improve the applicability of electrochemical testing for performance analysis purpose are discussed here. Literature review was conducted to understand the basic idea and implementation of these approaches. Segmented fuel cell, a physical device to probe performance distribution of PEMFC, is described in the first part. The rest of the chapter explains the Thin Film-Agglomerate Model, a theoretical approach to identify mechanisms that occur at the porous electrode of fuel cell.

3.1. Segmented Fuel Cell

Segmented fuel cell can be defined as a **fuel cell fixture** whose current collector is divided into several electrically isolated segments to facilitate in-situ and non-destructive spatially resolved electrochemical measurement. The development of this fixture is triggered by the performance distribution issue over the surface area of fuel cell, especially for large area fuel cell. Careful work by Natarajan and Nguyen (2004) had proven the existence of inhomogeneity of current generated over the cell surface, which is significant for optimum cell utilization as highly inhomogeneous performance would mean that there are some inactive parts of the surface-active area. Segmented fuel cell is then proposed to enable localized performance examination. This approach is also expected to be a useful tool for

model validation (Noponen *et al.*, 2004), and mechanism exploration. Schneider *et al.* (2007) used segmented fuel cell and sensor cell to perform key experimentation to understand the nature of low frequency arc for EIS at high current density.

3.1.1. Early Work on Spatially Resolved Measurement Design

Cleghorn *et al.* (1997) were among the first to work on current distribution investigation. This work was based on the use of Printed Circuit Board (PCB) to characterize current distribution in water electrolyzer. MEA arrangement was similar to current measurement for unsegmented fuel cell except that in their design, they segmented anode part from the current collector down to catalyst layer into 18 electrically isolated segments. The cathode side was left as a single piece of electrode. Figure 3-1 illustrates PCB and fixture configuration used in their experiment.

Figure 3-1 PCB and fixture configuration developed by Cleghorn *et al.* (1998)

This configuration used a switch to manage the connection between two loads. Measurement was done by uncoupling the segment observed out from the other seventeen. While the other segments were connected to first load box, segment under observation was connected to another load and its current was drawn by that load. Figure 3-2 below illustrates this connection setting.

Figure 3-2 Two loads connection setting for current measurement proposed by Cleghorn *et al.* (1998)

Stumper *et al.* (1998) offered three techniques to measure current density, namely partial MEA approach, sub cells approach, and current distribution mapping method, as shown in Figure 3-3. In partial MEA method, portions of MEA were tested individually. These portions could be prepared by either masking the area of the electrodes with PTFE or by using MEA whose electrodes were partially catalyzed. Sub cells in the second method were made by punching some holes out of the electrode and replacing them by the smaller ones (the gap was around 2 mm annular to isolate the sub cells from the main cell). Each sub cell as well as the main cell was controlled by separate load bank to enable adjustment of the respective cell current.

The third approach used passive resistor network, made from thin sheet of graphitic foil, inserted between electrode and current collector in appropriate location to map the current density. Current probe was placed prior to flow field or current collector since both have high electron conductivity capable of equalizing current generated at catalyst layer (Barbir, 2005). By measuring the potential difference across resistor, local current flow in that area could be calculated.

Figure 3-3 Sketch of three techniques introduced by Sumper *et al.* (1998)
(a) Partial MEA, (b) Sub cell, (c) Current mapping

The first approach seemed to be valuable only for steady state model validation and part-by-part examination. This method took longer time and required more effort to prepare the MEA. Real time observation for the whole area was not possible with this approach. Furthermore, this was not applicable for real fuel cell observation purpose since we need to divide MEA into several parts.

The second sub cells approach required MEA modification. Care had to be taken during hot press to assure that the anode electrode of the sub cell was well aligned with the cathode counterpart. Precise alignment of these electrodes was important since misalignment could increase cell resistance. On the other hand, this approach offered real time comparison among different located sub cells. This method also required multiple loads so that each sub cells can be controlled individually.

Current mapping approach, equipped with data acquisition system, also proven capable of carrying out real time measurement and was mentioned to be the most advanced method to obtain spatial current distribution. It can also cover examination for the whole area of the cell. The method had proven capable of capturing transient event like CO poisoning and its recovery (air bleed). One important thing is that the graphite used must be as close to MEA as possible to avoid current spreading.

Compared to the second approach, PCB approach by Cleghorn *et al.* also required modification in electrode. Several-times-bigger segment size compared to subcell approach made the MEA easier to prepare. In both methods, segmentation covered the whole cell and real time measurement was enabled. However, in Cleghorn's experiment (Cleghorn *et*

al., 1997), segmentation only proceeded at anode which could not hinder lateral current to occur.

Another consideration in PCB approach was about the use of two loads which involved coupling-decoupling among channels. There was no proof that the two loads would not interfere each other, especially when high voltage gradient occurred. In addition, coupling-decoupling activity was predicted to disturb steady condition for measurement. This means more time is required to obtain high-resolution measurement. The choice of using switch instead of data logging system, which avoided this setting to measure current simultaneously also contributed to longer measurement period.

These two pioneering works had set basis for further development of segmented fuel cell. Later works focused on segmented fuel cell modifications to achieve high measurement quality as explained in section 3.1.2.

3.1.2. Improvement on Segmented Fuel Cell Design

General consideration in segmented fuel cell is to retrieve signal of high resolution in order to obtain accurate description without over-disrupting the real time characteristics of the cell under investigation. In general, the design improvement comprises of reduction of lateral current and measurement architecture.

3.1.2.1. REDUCTION OF LATERAL CURRENT

In order to obtain high data resolution, it is desirable that electron generated in particular segment travels in direction perpendicular to MEA and lateral current be minimized. This

lateral current, i.e. spreading of current over the gas diffusion layer and current collector surface parallel to MEA, highly reduce the measurement resolution as current registered as originated from one segment involves significant contribution from current generated in other parts. The lateral current occurs due to high in-plane conductivity and high variation in contact resistance causing steep potential gradient over the conducting surface parallel to MEA. Considering that high in-plane conductivity is inherent characteristics of GDL and current collector material which is difficult to modify, two groups of opinion were formed. The first group suggested that the electrodes (GDL and catalyst layer) should be segmented to avoid this problem. Another group raised its objection as segmentation in electrodes altered the real mechanisms occurred in real fuel cell such as reactants and charge transport.

Segmenting both electrodes down to the catalyst layer definitely reduces current spreading as boundary among segments is clear. This approach was actually implemented by Cleghorn *et al.* (1997) even though they only segmented the anode side. However, the MEA preparation can be very exhausting. Misalignment in electrode for example, can increase cell resistance significantly. Hakenjos *et al.* (2004) suggested partially segmented MEA to address this issue (illustrated in Figure 3-4). This was done by etching GDL to make 0.2 mm wide gap to increase in-plane resistance as high as 0.5 Ohm. Nevertheless this increase in in-plane resistance in this method was considered too small to minimize current spreading.

Natarajan and Nguyen (2004) were among the first who applied segmented electrode for both anode and cathode. Their design at first was dedicated to verify the existence and extent of current dispersion within a common GDL in contact with multiple isolated

current collectors. Their observation revealed that segmented electrode could give consistent result at both potentiostatic and galvanostatic modes while common electrode (unsegmented GDL) only at potentiostatic mode. This is to say that they suspected current spreading occurred in common electrode mode due to anisotropy condition of GDL and would significantly affect the measurement resolution.

Figure 3-4 Partially segmented gas diffusion layer proposed by Hakenjos *et al.* (2004)

On the contrary, the studies done by Noponen *et al.* (2002) suggested that current spreading would only occur in small extent over the surface of unsegmented electrode. When they calculated current density for their experiment result using non-segmented electrode, they assumed that each segment of current collector would collect current from regions of equal size. This meant adjacent regions would have imaginary division line right in the center between these two. To validate their assumption, they used Femlab to study four neighboring regions of an unsegmented electrode area (without actually dividing it). One part was simulated to produce current 50% lower than the other. They expect that if cross talk affected the current measurement significantly, the virtual division line between the regions would distort notably indicating distortion of voltage profile within the electrodes.

The outcome showed that despite the large current gradient applied, the virtual division line among the four parts was shifted only slightly from initial centerline, leading to small deviation of contact area. This meant that even under that high variation in local current distribution, current distribution profile did not change significantly. Therefore, they concluded that locally resolved current measurement can still be carried out with reasonable accuracy even when the cell electrodes were not segmented but contact variations should still be minimized. In comparison to the result of Natarajan and Nguyen (2004), this simulation did not account for assumption on GDL in-plane conductivity which is several times higher than its through-plane conductivity even though they introduce reasonably large overpotential to compensate for it.

Wieser *et al.* (2000) was in agreement with the second group to leave the electrode unsegmented for spatial registration. They proposed the use of contactless magnetic array with Hall sensor to minimize the variation in contact resistance. The sensor was inserted into annular ferrite. This ring was then positioned between current collector and flow field, as can be seen from Figure 3-5. Their experiment indicated that bracing pressure resulting from inner and outer bracing screws gave strong influence on electrochemical performance. Unfortunately, further information about the bracing was not given. Disadvantage of this method is that current measurement from one segment could include participation from neighborhood current due to the characteristics of Hall sensor used. To minimize this problem, they suggested sufficient distance from one segment to the others which cause big segment size (38 mm x 38 mm). This method would not be appropriate for small PEMFC. Insertion into stack, by considering bracing pressure above, will also cause some problems.

Figure 3-5 Hall sensor application in magnetic loop array for current measurement

Bender *et al.* (2003) solved segment dimensions and Hall sensor-neighboring segment interaction by locating the sensor within special constant temperature housing at certain distance from the cell. Constant temperature was needed to avoid drift and offset. The arrangement of placing Hall sensor outside the fixture reduced the fixture thickness, which means reduce in pressure needed to sustain good contact resistance.

Mench and Wang (2002) acknowledged that current spreading does occur at diffusion layer. However, they highlighted that it was desirable to utilize a non-segmented MEA to avoid disturbance in water and species transport as well as to avoid difficulty in MEA preparation. In response to the current spreading issue, they modified current distribution mapping technique introduced by Stumper *et al.* (1998) and applied it to Direct Methanol Fuel Cell (DMFC). Instead of using resistor network to probe current, they used electrically segmented flow field–current collectors. Flow fields were etched to transparent polycarbonate plate and embedded ribs connected to current collector were gold plated to obtain good electrical contact. In this design, current collector was in direct contact with gas diffusion layer, which helped minimize current spreading due to in-plane conductivity of flow field as noted by Stumper *et al.* (1998). In addition to that, repeatable measurement can be easily conducted. The design is shown in Figure 3-6.

Figure 3-6 Transparent fuel cell with segmented gold plate current collector ribs proposed by Mench and Wang (2000)

3.1.2.2. MEASUREMENT ARCHITECTURE

Included in this consideration is whether the measurement will be carried out in sequential or simultaneous mode. The choice in the measurement mode will affect the choice of load and complication of the device setting. Usually the first mode involves switch utilization to control scanning route. The load can be one or two loads as exemplified by Cleghorn *et al.* (1998). This mode is simpler and suitable for steady state measurement.

The second mode will significantly outperform the first in terms of speed. This setting is also capable of accomplishing real time and fast process measurement. To fulfill its function, the arrangement required sophisticated measurement setting. Individual control is also needed to avoid potential-driven lateral current. In relation to this problem, Mench-Wang and Hakenjos *et al.* agreed to use multipotentiostat to regulate potential of each segment. By equaling their potential, “cross talk” among segments can be minimized.

Even though there are many methods used to measure current, they share the same principle to collect current or voltage data. The other principle rarely used was by

measuring magnetic flux surrounding fuel cell (Magneto-tomography). This principle was applied to a prototype designed by Hauer *et al.* (2005) who used 3D magnetic flux sensor to determine current by simultaneously solving Maxwell equation for 36 segments. The difficulty laid in data processing step because the magnetic flux for one segment carried signal from the other segment. Therefore, accurate assumption was needed to perform calculation. The outcome of this method has not been reported yet.

3.1.3. Application of EIS to Segmented Fuel Cell

When Cleghorn *et al.* (1998) introduced PCB technique to analyze current distribution, they also carried out measurement on High Frequency Resistance to explain relationship between water balance with current distribution. In their experiment, they supplied 0.04 V peak to peak perturbation to measure high frequency resistance (HFR) at frequency 8 kHz. Their results are illustrated in Figure 3-7. Strong reciprocal relation between current and HFR can be observed as current density decreased when (HFR) increased. They concluded that increase in membrane dehydration as indicated by increase of HFR caused by poor proton transport. However, more investigation needs to be carried out as there were some segments (especially early segments) deviating from this relation.

Experiment conducted by Bender *et al.* (2003) utilized impedance spectroscopy but merely to determine the contribution of experimental setup to the measured cell response. Their results detected the presence of inductive component within the spectrum response. They predicted that the inductive component originated from Hall sensor transfer function and contribution of system wires. They suggest calibration to eliminate those parasitic elements. This conclusion was in agreement with recommendation given by Vladikova (2004).

Figure 3-7 Current and high frequency resistance distribution experiment for H_2/O_2 using Nafion™ 117 membrane, Cleghorn *et al.* (1998)

EIS to probe impedance distribution over the segments was recently utilized again by Hakenjos (2004). Combined with current and visual measurement, they managed to explain the correlation between temperature, water flooding, and current generated. Similar to Cleghorn's, EIS utilization was mainly focused on HFR distribution. On the other hand, Ciureanu (2004) argued that HFR consisted of resistance from wire and connection, cell component, and interface contact among components. That is to say more information should be taken into account to achieve higher process identification accuracy.

Schneider *et al.* (2005) extended application of EIS further by taking resistance of electron transfer (R_{et}) into their performance analysis using segmented fuel cell. They observed current distribution and the frequency spectrum of serpentine topology cell while it was running on co-flow mode. The result showed that there was strong correlation between

water content, HFR, and R_{et} . They suggested that the lack of water at Nafion ionomer and catalyst interface would cause increase in diameter of the kinetic arc.

Many studies have shown that EIS is a powerful tool to identify mechanism within electrochemical system. This technique has also proven to be powerful to identify mechanisms in PEM Fuel cell. Parthasarathy *et al.* (1992) utilized EIS to investigate dependency of oxygen reduction kinetics at platinum/Nafion interface on oxygen partial pressure at ambience and elevated temperature. Springer *et al.* (1996) made thorough analysis about effect of PEM fuel cell component on impedance spectra, which lead to diagnostic criteria to evaluate PEMFC losses. Thorough investigation by Ciureanu *et al.* (2004) showed that EIS was reliable to reveal potential deterioration mechanism when different humidification schemes applied.

On the other hand, not much attention has been given to EIS-applied to-segmented fuel cell for performance assessment purpose. Only small number of papers is available to discuss EIS contribution in locally resolved measurement. In addition, interpretation of response obtained is often difficult. However, by considering its potential, this project will pose EIS-segmented fuel cell arrangement as one of its focus in identifying and analyzing mechanisms affecting the performance of PEMFC.

3.2. Thin Film-Agglomerate Model

3.2.1. Overview

As mentioned previously in Chapter 2, impedance is an information property of a system. Therefore, modeling is required as a platform in interpreting the data and correlating the information with the physical phenomena occurring within the object of interest. Several EIS models suitable for PEM Fuel Cell were briefly reviewed in Chapter 2. This section will discuss the Thin Film/Agglomerate model which capable of providing complete illustration of fuel cell porous electrode. The model covers Faradaic process, the interaction between catalyst agglomerate and electrolyte, as well as transport in gas diffusion layer. This approach is valuable to study the mechanism in the cathode as well as extracting different parameters to separate different parasitic losses from impedance data. The domain of interest in this model is given in Figure 3-8 below.

Figure 3-8. Illustration of Thin Film-Agglomerate model (Springer and Raistrick, 1989)

There are two regions of concern in this model. Agglomerate region is illustrated physically as finely divided interconnected network of electrolyte-filled carbon with interspersed catalyst and mathematically as a uniform region of thickness L with a diffusion coefficient D_a . In this region, electron is produced in the catalytically

microporous region. On the thin film side, reactant diffuses from bulk gas region through a layer of electrolyte that covered the agglomerate region of thickness δ in which no catalyst is presence. The properties of these two regions are summarized in Table 3-1.

In the illustration above, impedance for thin film diffusion in series with impedance for agglomerate reaction and diffusion makes up the total impedance for the interface. This series of impedance is in parallel with double layer capacitance as the result of charge redistribution at the electron-proton conducting interface and electrolyte resistance is added to equivalent circuit. Those properties in this model have different characteristic frequency and dependence of overpotential.

Tabel 3-1 Properties of the thin layer and agglomerate regions

Agglomerate Region	Thin Film Region
Physically finely divided interconnected network of electrolyte-filled carbon with interspersed catalyst	A layer of electrolyte covering the agglomerate region
Reaction occurs at catalytically micro-porous region	No reaction (no catalyst), diffusion of reactant from bulk gas region
Impedance Z_A Diffusion coefficient D_a Thickness of L	Impedance Z_D Diffusion coefficient D_f Thickness of d
Governing equation: for $0 \leq Y \leq L_y$: $-\frac{\partial c}{\partial t} + D_a \frac{\partial^2 c}{\partial Y^2} = \frac{k^o}{L_y} ce^\mu$ $BC : D_f \frac{\partial c}{\partial Y}(-0) = D_a \frac{\partial c}{\partial Y}(+0); \frac{\partial c}{\partial Y}(L_y) = 0$	Governing equation: for $-\delta \leq y \leq 0$; $-\frac{\partial c}{\partial t} + D_f \frac{\partial^2 c}{\partial Y^2} = 0$ $BC : c(-\delta) = 1; c(-0) = c(+0) = c_o$

As any other fuel cell impedance model, this model is applicable to study the cathode performance. This is because kinetics and mechanisms occur at anode are significantly

simpler thus far faster. As the result cathode performance limits the overall cell performance. Two-electrode measurement with four-probe for resistance compensation is thus sufficient for EIS measurement as suggested by Ciureanu (1999). With this arrangement, anode acts as a reference as well as counter electrode.

Based on this model, EIS measurement should produce three arcs; loop at the highest frequency correlates with the charge transfer resistance in oxygen reduction reaction and the diffusion of oxygen through the electrolyte, middle frequency arc shows the dynamic of the agglomerate, and the low frequency arc shows the hindrance for diffusion in thin film region. In actual experiment condition, rarely are these three arcs seen. One reason for this situation is the experimental condition impedes certain resistance mechanisms to occur. Masking effect can also avoid some arcs to appear when the semicircle with similar time scale or process with large capacitance appears.

According to this model, transport limitations occur in cathode catalyst layer. It is found that as the cathode overpotential increase, the resistance for agglomerate diffusion reduces while the resistance for thin layer diffusion increases. There are still discrepancies over which mechanism limits cell performance at low frequency. Researchers are not yet in agreement on whether diffusion of oxygen to reach catalyst layer, water back diffusion in membrane, or water diffusion the backing correlates with low frequency arc at high overpotential. Few experiments have been conducted to investigate phenomena at low frequency to verify the mechanism.

Paganin *et al.* (1998) highlighted the success of thin film/agglomerate model to explain the mechanisms for hydrogen fuel cell whose response is dominated by cathode performance and very low anode overpotential can be expected. This model has been capable of predicting the effect of various operating cell parameters to cell impedance. Mechanisms captured in by incorporating this model into EIS measurement is:

- polarization resistance due to ORR which is parallel to capacitance double layer
- distributed resistance due to the ohmic drop in the electrolyte of catalyst layer
- limiting concentration gradient of oxygen in the flooded-agglomerate
- limiting concentration gradient of oxygen in the thin film
- diffusion of oxygen in gas diffusion electrode when air is used instead of oxygen

Mechanisms above have different characteristic frequencies for certain operating parameter. In general, charge transport in the catalyst layer will dominate total process at high frequency (>100 Hz) while mass transport in GDL, catalyst layer, and membrane is important at low frequency (< 0.01Hz) (Gomadam and Weidner, 2005).

3.2.2. Mathematical Aspect of Thin Film - Agglomerate Model

Full mathematical derivation for this model was provided by Springer and Raistrick who introduced this model back in 1989. Based on this model, Ciureanu and Roberge (2001) introduced the diagnostic equation below to distinguish the presence of different mechanisms by identifying the reduced resistance R/R_o :

$$\frac{R}{R_o} = 2 \frac{1 + \Gamma e^{\mu} \gamma}{[(\sigma + \gamma)e^{\mu}]} \quad [3-1]$$

where

R = Resistance obtained from the low frequency limit ($\omega \rightarrow 0$)

R₀ = Resistance at limiting current density

$$\mu = \frac{\eta_c}{b'} \text{ (reduced overpotential, with } b' = \frac{RT}{\alpha n F} = \text{Tafel slope)}$$

$$\Gamma = \frac{\delta k_o}{D_f} \text{ is the parameter defines the thin film diffusion}$$

$$\Phi = \left(\frac{k_o L_y}{D_a} \right)^{1/2} \text{ is the agglomerate diffusion parameter}$$

$$\gamma = \frac{\tanh(\Phi e^{\mu/2})}{\Phi e^{\mu/2}}$$

$$\sigma = \sec h^2(\Phi e^{\mu/2})$$

The use of this model for mechanisms identification purpose stemmed from the observation of charge transfer resistance and diffusion resistance as a function of cathode potential. Therefore, in order to obtain the full description of a system, registration of potential, current, and impedance over a broad range of potential to explore the agglomerate and thin film dynamic is required. There are two conditions considered in this equation.

3.2.2.1. ACTIVATION REGION/CONDITION WITHOUT DIFFUSION LIMITATION

In Chapter 2 it was mentioned that Butler-Volmer equation for cathode which requires relatively high overpotential at activation region is expressed as:

$$\eta = -\left(\frac{RT}{\alpha n F} \right) \ln i_o + \left(\frac{RT}{\alpha n F} \right) \ln i \quad [2-5]$$

In activation region, it is assumed no diffusion limitation therefore the effective concentration at the surface of the catalyst layer can be assumed to be the same with the bulk concentration ($C_R^* = C_R$).

With $b' = \frac{RT}{\alpha n F}$, equation 2-1 changes into

$$\eta = -b' \ln(i_o) + b' \ln(i) \quad [3-2]$$

$$\eta = b' \ln\left(\frac{i}{i_o}\right) \quad [3-3]$$

or

$$\eta = b' \ln\left(\frac{R_o}{R_p}\right) \quad [3-4]$$

R_p surfaces since the loss in activation region is due to parallel resistance with the double layer capacitance. In other word, $R_p = R_{ct}$

Introducing $\mu = \frac{\eta}{b'}$, equation C-3 now becomes:

$$\frac{R_p}{R_o} = \exp(-\mu) \quad [3-5]$$

In agreement with the assumption for Butler-Volmer equation solved for cathode activation, no diffusion losses occurs yet (particularly in thin film), therefore $\Gamma = \Phi = 0$ hence $\gamma = \sigma = 10$

Inserting those values setting for no diffusion condition into equation 3-1,

$$\frac{R}{R_o} = \exp(-\mu) \quad [3-6]$$

From equation 3-4 and 3-5, we obtain that $R = R_p$. This means that if plot of V_{cath} as a function of $\log(R_p^{-1})$ is drawn, the slope of this line will be $b = 2.3 b'$. Derivation of this correlation roots from equation 3-3 by substituting $V_{cath} = E_o - \eta$ to obtain

$$V_{cath} = E_o - b' \ln\left(\frac{R_o}{R_p}\right) = E_o - b \log\left(\frac{R_o}{R_p}\right) \quad [3-7]$$

$$V_{cath} = [E_o + b \log(i_o)] - b \log\left(\frac{1}{R_p}\right) \quad [3-8]$$

It is worth to note that iR_Ω factor (loss due to ohmic resistance) is required to make correction for the cathode potential from cell potential:

$$V_{cath} = V_{cell} + iR_\Omega \quad [3-9]$$

The schematic diagram of the potentials and its correlation with losses in polarization curve is shown in Figure 3-9.

Figure 3-9 Schematic diagram of decrease from E_{rev} and corresponding losses

3.2.2.2. AT LARGER OVERPOTENTIAL/CONDITION WITH DIFFUSION AS LIMITING FACTOR

When magnitude of the slope obtained from the plot V_{cath} versus $\log R_p^{-1}$ is different from b

$= 2.3 \left(\frac{RT}{anF} \right)$, other process determining cell condition can be expected. This condition

occurs at larger potential where demand of reactants supply is higher compared to first scenario. When thin film diffusion is considered to be negligible, which is translated to diagnostics equation 3-1 above as $\Gamma = 0$, equation 3-1 becomes:

$$R = \frac{2R_o}{e^{\mu}(\sigma + \gamma)} \quad [3-10]$$

As the consequences, value of R_p will decrease with the increase of overpotential. At this condition, when we plot the V_{cath} vs $\log (R_p^{-1})$, the slope obtained here will be doubled than that at low overpotential.

When the overpotential is further increased, the term Γ will become non-negligible and larger slope value can be expected as the thin film effect becomes more prominent.

Even though Thin Film-Agglomerate Model is considered to be a powerful model in determining the performance limiting factor in fuel cell, works dedicated to use this model as a platform to analyze the fuel cell performance were relatively few. Therefore, one part of this project will be dedicated to explore the capability of this model to perform model-based mechanism identification in PEM Fuel Cell.

Experimental Setup

In general, experimental setup consists of Membrane Electrode Assembly, fixture, fuel/oxidant humidification and distribution, and measurement devices. Two kinds of fixture, segmented and non-segmented fixture, were used to conduct the measurement. The MEAs for experiment were prepared in house and the steps to prepare them are explained in section 4.2. The last part of this chapter explains the testing station consisted of gas handling unit and measurement devices.

4.1. Preparation of Cell Fixtures and Current Collector

4.1.1. Segmented Fixture

The design for the segmented fixture was prepared by taking into account the design consideration explained in Chapter 3 to conduct locally resolved performance registration for PEM Fuel Cell. Special fixture is made from 1.5 cm thick polycarbonate (isolator material), 10 cm x 10 cm in size. The inner and outer surfaces of the fixture are shown in Figure 4-1. Sixteen graphite blocks (1 cm x 1 cm at the inner side) placed in the middle of fixture plate in 4 x 4 arrangement are embedded into the polycarbonate to collect current (AA – BB area). 2-mm gap between graphite blocks is to give electrical isolation between them. The dimension of outer side of each probe block is 0.8 cm x 3.6 cm with two-1 mm diameter holes each to carry out measurement and electrical connection. This surface also has two gas connections to transport reactants and products. Support to obtain homogenous

pressure distribution is given by two 6-mm thick stainless steel plates at both sides of cell. This design mentioned above applied to both anode and cathode fixture. Dimension of MEA used in the whole experiments is 16 cm² in geometric area. No MEA segmentation is applied to both anode and cathode.

Figure 4-1 (a) Inner surface / flow field side of the fixture, (b) Outer surface / probe side of the fixture

Flow field 1 mm wide and 1 mm deep is machined in the inner surface of the fixture. Three types of topology were used for the experiment: single path serpentine (1-S), parallel (P), and 3-path serpentine (3-S). Each tip of the flow field at inner surface of fixture is directly connected to gas connection at outer surface through the thickness of the fixture. Parallel geometry consists of 25 lines adjacent one another and the end of each the line allows fluid within to flow through one out of two branches. The 1-S flow field had dead ends that dictated the reactants to flow in only one direction at the inner surface of the fixture. The 3-S flow field had both Parallel and 1-S characteristic since each three line in a group were in parallel and bent together similar to 1-S arrangement. Drawings for those flow fields as well as the image of the fixture with switch network are given in Appendix A.

4.1.2. Non-Segmented Fixture

The second fixture was a non-segmented fixture consists of 1 cm thick graphite plate and stainless steel of the same thickness at each side of MEA. The graphite plate is 5 cm in width 8 cm in length with 1-S topology etched at the inner surface contact with GDL, responsible for gas distribution over the GDL surface. The size of MEA fit for this fixture was 2.5 cm x 3 cm and was prepared in the same method as the MEA for the segmented fuel cell. The outer surface of the graphite plate is in contact with 8 cm x 8 cm x 1 cm steel plate where heat transfer media can flow through its thickness to facilitate thermal control for the cell. 4-mm holes are drilled in each plate, both graphite and stainless steel to mount current and voltage probe. Bolts to clamp the cell are placed in the corner of stainless steel plate with 1 mm thick plastic casing to avoid short circuit between anode and cathode. Figure 4-2 shows the assembly of non segmented fixture for single cell assembly.

Figure 4-2 Single cell assembly with non segmented fixture

4.2. Preparation of MEA

In general, there are two methods to prepare MEA. The first is PTFE bound method which spreads the ink into gas diffusion layer. The second is thin film method which applies catalyst ink into membrane. MEAs used in the experiments explained here were fabricated via modified PTFE bond method. The difference between original and modified PTFE bond method rests in how ionomer is impregnated onto the catalyst layer. In the original method, ionomer is brushed onto sintered diffusion layer which has catalyst ink applied prior to sintering step. In modified PTFE bond, the ionomer solution was added into the catalyst ink and the ink was sequentially applied to carbon paper/gas diffusion layer prior to sintering step. The benefit of the later method lies in ease to control Nafion content in the catalyst ink.

4.2.1. Membrane Preparation

Membrane used in this experiment is a 50 μm thickness Nafion® 112, perfluoro-sulphonic acid membrane. This transparent membrane need to be treated with 5% hydrogen peroxide (aqueous) solution at the solution boiling point to oxidize organic impurities. Deionized water is used to rinse the membrane several times afterward to clean any remain hydrogen peroxide. The membrane needs to be immersed in hot diluted sulfuric acid to remove any metallic impurities. The last step is to treat the membrane several times in boiling deionized water to remove traces of acid. The membrane is immersed in deionized water for storage purpose.

4.2.2. Catalyst Preparation

Catalyst used is 40% weight carbon-supported platinum catalyst (the catalyst size is about 2 – 3 Å) obtained from DeNora North America Inc., E-TEK division. One characteristic of the platinum is it is not compatible with any strong oxidizer and organic material. Therefore, water is needed as a solvent and is added prior to addition of Nafion ionomer to avoid exothermic reaction between catalyst and the ionomer which will damage the catalyst.

After weighing catalyst Pt/C according to catalyst load intended, some water is added to cover the surface of the catalyst powder to avoid catalyst damage. Nafion ionomer solution (5%) is then added over the water covered catalyst mixture with ratio solution to Pt/C equal to 3:7. Water and isopropanol are put into the mixture prior to stirring step. Both magnetic and ultrasound stirring are used to obtain sufficient viscosity and homogeneity.

4.2.3. Gas Diffusion Layer Preparation

Gas diffusion layer used here is carbon paper 250 µm in thickness, coated with PTFE (30%) to enhance its hydrophobicity. The GDLs are cut and weighed as needed based on catalyst loading target. Carbon powder solution is prepared by mixing carbon powder with PTFE in 7:3 ratio. This carbon powder will improve pore homogeneity. Water and isopropanol are added prior to stirring to control the viscosity of the solution. The amount of water added is nearly the same as that of PTFE and the amount isopropanol in the solution is around 30% of water added. After homogeneous mixture is obtained, the mixture is then applied and the GDLs are subsequently dried in ambient temperature. This step is repeated several times to obtain loading of about 2-3 mg/cm². After overnight

drying at ambient temperature, the GDL was then sintered in the oven for about one hour in 400°C. Subsequently the GDL is then weighted to check the carbon paper loading. Visual check is necessary to assure no crack on the surface.

4.2.4. Assembly of the MEA

The assembly step consists of catalyst application onto the GDL, hot press to merge membrane and electrode, and sealing. The first part is done by painting the catalyst ink over the carbon paper, drying it and sinter the GDL with catalyst for about 30 minutes in oven at 130°C. The next step is the assembly of membrane and electrode via hot press at 30 – 40 kg/cm², 130°C for around 1.5 minutes. The applied pressure scales with surface area and considers the weight of the sample (MEA) holders. To prevent gas leakage, two pieces of 250 µm silicon elastomer are arranged to cover parts of the membrane which are the fringes of GDL area. Figure 4-3 shows the picture of MEA sealed by silicon gaskets.

Figure 4-3 MEA sealed by silicon gasket

4.3. Testing Station

4.3.1. Gas Handling Unit

Hydrogen of concentrations 99.5% (nitrogen as the balance) was flown into the anode gas inlet as the fuel. Pure oxygen or its mixture with nitrogen (air) reacted at cathode side. Nitrogen was used to test leakage and clear the gas channel from any blockage prior to each measurement. This gas was also used to purge the cell prior to and after the test. All gases were obtained from Singapore Oxygen Air Liquide Pte. Ltd.

Each gas (dry gas) discharged from gas cylinder was channeled through GlobeTech PEM fuel cell testing station capable of switching gas between hydrogen-nitrogen at anode and oxygen-nitrogen-air at cathode. Bronkhorst mass flow controller was used to adjust reactant rate entering the cell. Gas humidification was done by bubbling method, i.e. the gas was introduced to water chamber and the contact resulted in increase in gas humidity. GlobeTech Fuel Cell Testing Station, shown in Figure 4-4, handled this inlet treatment. This device is also capable of adjusting the extent of gas humidification by controlling the temperature of water chamber. This testing station also provides bypass line permitting gas to flow without passing humidification section. Back-pressure valve for each anode and cathode side can be adjusted to elevate cell pressure. Experiments reported here ran at atmospheric pressure thus back pressure control was not necessary. Figure 4-5 illustrates schematic diagram of measurement setup.

Figure 4-4 Testing station (PS-CompuCell™, Globetech) for segmented fuel cell registration

Figure 4-5 Schematic diagram of measurement set up

4.3.2. Testing Devices

Autolab PGSTAT 30 and Solartron 1470E equipped with the module 1255B were used in this project. Both are capable of performing current and impedance measurement but are of different current range. Autolab's PGSTAT 30 from Eco Chemie BV (Figure 4-7 (a)) along with its software (Fra and GPES v4.9) were used to collect data from segmented fuel cell experiment. This single channel potentiostat/galvanostat device can measure current only up to 1 Ampere. 10-Ampere booster module (BSTR10A) was integrated to PGSTAT 30 to facilitate measurement for 16 cm² electrode. Additional manual switching unit was hence needed to perform locally resolved measurement.

Even though Solartron 1470E is specially designed to handle current measurement for 8 channels in parallel (multichannel measurement) as it uses electromagnetic switch, this device was use only for single current measurement due to technical problem encountered and currently is still in investigation. Its power amplifier is able to provide continuous output voltage in the range +10V to -3V or current in the range of +4A to -4A, which is suitable for smaller cell (7.5 cm²). In order to conduct EIS measurement, this device has to be connected to Solartron 1255B (frequency range 10 μ Hz to 1 MHz) through the Ethernet port. The Solartron 1470E and Solartron 1255B are shown in Figure 4-6 (b) and (c).

Figure 4-6 (a) PGSTAT 30 equipped with 10A booster for EIS registration
(b) Solartron 1455E multichannel potentiostat/galvanostat (c) Solartron 1255B Frequency Response Analyzer

4.3.3. Multiplexing

The general principle of multiplexing is shown in Figure 4-7. In this figure, red line represents the working electrode (cathode), black represents counter electrode, yellow for sense electrode (reference for working electrode), and green is the reference electrode.

Figure 4-7 Schematic Diagram of Segments Multiplexing

Manual multiplexing was accomplished by using eight SPST (Single Pole-Single Throw)-on-off type switch to conduct measurement. This switch network connected all the segments together at activation stage or when total cell measurement was conducted. The anode reference wire of each segment were connected together to form common anode reference. The same applied for the cathode. With this configuration, when one particular segment was observed, the other segments signal would not be measured but they would be connected to common reference terminal. The potential of this common terminal was controlled by the reference of the testing device. The importance of this common reference is to maintain isopotential condition among the segments. As discussed in Chapter 3, this

isopotential condition is important to assure minimum cross no crosstalk from one segment to the others especially for the unsegmented electrode.

4.4. Experiment Procedure

4.4.1. Cell Pretreatment

To achieve relatively similar starting point for each sets of measurement, standard procedures below were performed before collecting the data.

1. LEAKAGE TEST

To assure no performance loss caused by leakage, nitrogen was fed to the cell as testing fluid after the completion of fixture assembly. Liquid soap for leakage detection purpose was used and bubble would be released if nitrogen happened to escape from a particular (usually joint) spot. The gas flow was adjusted to operating flow rate to assure that the cell will work at specified experiment.

2. PURGING THE CELL WITH HUMIDIFIED NITROGEN

This step was performed with three different flow rates. The length of time for purging as well as the flow rate depended on the size of the MEA as well as the purpose of the subsequent measurement but in general this was done in two steps. The first step supplied higher flow rate to clear the path in gas diffusion layer. Subsequent purging applied lower flow rate to allow water to diffuse and hydrate the membrane.

3. OPEN CIRCUIT VOLTAGE OBSERVATION

Detail on ideal and actual open circuit voltage (OCV) was discussed in Chapter 2. Generally OCV value above 0.9 V is acceptable for cell running on pure hydrogen and oxygen at 1 atm. For segmented fuel cell, it is also necessary to assure that all segments give OCV standard deviation-to-average range within about 5% to assure

homogeneous condition over the membrane-electrode-gas interface. OCV reading was taken not earlier than fifteen minutes after reactants flowed through flow field to ensure steady state measurement.

4. CELL ACTIVATION

Prior to data acquisition, the cell ran at certain point of potential depend on the operating potential needed in total duration 2 hours. This is usually 0.6 V and 0.4 V for 2 hours duration, 2 x 30 minutes at each potential. The importance of this step was to assure electrochemical and transport activity within the cell had reached steady state since the focus of this experiment was to obtain steady state current distribution of PEMFC. This step was skipped in some type experiments, depending on the objective in that particular experiment.

4.4.2. Measurement

1. CURRENT MEASUREMENT

Current data of all segments were collected at potentiostatic mode using four probe connection. Polarization curve was obtained by setting step mode at certain potential for 30 second.

2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Four probes were extended from EIS hardware to conduct measurement with cathode as working electrode and anode as the counter electrode, as well as reference electrode due to its high hydrogen oxidation reaction rate. The whole measurements ran in potentiostatic mode. FRA module generated signal and analyzed the resulting current to obtain impedance data.

Impedance measurement was carried out in single sine or 15-sine mode. This 15-sine mode offered higher measurement rate compared to single sine mode. However, at high overpotential, single sine offered better resolution compared to 15-Sine mode. Frequency range of 0.1 – 10 kHz was chosen as it covers the phenomena observed in for this project. To assure linearity of the response, 10 mV perturbation was chosen and supplied to the cell.

Results & Discussion

This chapter is devoted to discussing the experimental results obtained in order to evaluate and improve performance analysis capability of Current Measurement and Electrochemical Impedance Spectroscopy (EIS) techniques. Two relatively new approaches, segmented fuel cell and Thin-Film/Agglomerate model, were incorporated into these two established techniques to improve the mechanism identification as a part of the fault detection scheme. The experimental results obtained by the application of these two approaches were presented in the first two sections. The last section deals with water related mechanisms and their characteristics in current and impedance response. In addition to the explanation on the outcome of the experiment, this chapter will also discuss some technical aspect of data acquisition, especially related to EIS.

5.1. Application of Current Measurement Method and Electrochemical Impedance Spectroscopy to Segmented Fuel Cell

5.1.1. Application of Current Measurement Method to Segmented Fuel Cell

The first part of the experiment observed the spatially resolved current measurement using segmented fuel cell fixture to monitor the effect of cell design and operating parameters on cell performance distribution. Both sides of the cell fixture were segmented into 16 parts as explained in Chapter 4. To facilitate data analysis, location of each segment of the cell marked with number 1 – 16 is given in Figure 5-1. This figure illustrates the view of

cathode side where oxygen inlet was located at the top right corner while the exit was at bottom left corner. On the other hand, hydrogen in the anode was arranged in different manner, i.e., inlet at bottom right corner and exit at top left corner. Unless otherwise stated, streams in all series of experiment flow in serpentine manner.

Figure 5-1 Segment numbering for 16-segment mode

In this set of experiment, the cell performance was tested using three different flow fields to understand the effect of cell design on the spatial current generation. Flow rate was chosen to be 350 sccm for hydrogen and 175 sccm for oxygen following the stoichiometric requirement. The reactants passed the humidification chamber at room temperature. Therefore, the reactants humidification level was expected to be low. Water content of polymer electrolyte membrane which plays an important role for proton conduction, as explained in Chapter 4, was supplied by low flow rate humidified nitrogen at purging step as well as by water generation reaction at activation step.

5.1.1.1. OPEN CIRCUIT VOLTAGE AT INITIAL STAGE

Before the measurement proceeded, distribution of Open Circuit Voltage over the segments was observed. The registration of OCV served as an indicator showing whether

the contact resistance was sufficiently low and even among the segments. As explained in Chapter 3, uneven contact resistance can lead to current spreading or “cross talk” hence reducing the measurement accuracy.

Prior to each experiment conducted, OCV value for each segment was taken. Standard Deviation (σ) was used to evaluate segments’ OCV which describes how clustered OCV values were distributed around the average value. The expression for σ is given by

$$\sigma = \sqrt{\frac{1}{N-1} \sum (x_i - \bar{x})^2} \quad (5-1)$$

Table 5-1 below presents the standard deviation calculation of OCV for this set of measurement. Value of 0.005 (around 0.5%) was chosen as the maximum allowable deviation for contact uniformity of the fuel cell assembly. If the average of absolute deviation calculated from the 16 segments exceeded this value, fixture assembly were rechecked for contact resistance and leakage.

Table 5-1 Inspection on OCV homogeneity over the cell for different flow fields at 350 sccm H₂ and 175 sccm O₂

Flow Field Parameter	Parallel	1-S	3-S
Average	0.9901	0.9730	0.9750
StDev	0.003	0.002	0.001
StDev/Ave	0.0027	0.0017	0.0013

According to the Nernst equation, high reactants supply due to high flow rate, (thus high reactants partial pressure) would give rise to high OCV value for all flow field designs. The average OCV value of parallel topology was the highest among other flow field

topologies. 3-S topology was in the second place but its OCV value was not far different from 1-S value. This sequence implicitly means that both reactants in parallel topology can reach reaction sites easier than other topologies. The probable reason for this is small pressure drop developed by parallel topology best facilitate reactants to reach active sites at condition when water is not yet produced. It is worth to note that OCV measurement was registered prior to cell activation. In subsequent discussion, in contrast to the OCV trend obtained, it was observed that parallel flow field generated the lowest current compared to other flow fields.

The highest value of the ratio of standard deviation to average value in the parallel flow field indicates the highest non-homogeneity among the three topologies used in this experiment. Figure 5-2 plots OCV patterns generated by these flow fields. The same phenomena were also found in the current measurement showing uneven performance distribution over the cell. Pressure distribution exercised by parallel topology is probably the cause for this. Explanation related to pressure distribution is given in later section for the effect of parallel topology on performance distribution.

Figure 5-2 OCV of Parallel, 1-S, and 3-S flow fields, operated at 350 sccm H₂ and 175 sccm O₂

The ideal value for OCV is 1.23 V when liquid form of water comes out as product. As can be seen from the graph, average OCV value for Parallel, 1-path Serpentine (1-S), and 3-path Serpentine (3-S) are 0.990 V, 0.973 V, and 0.975 V, respectively. Those values are acceptable as their magnitude all exceeding 0.9 Volt, which is considered to be practical value for PEM fuel cell. Around 0.19 – 0.21 V was lost most likely due to reactants crossover through electrolyte and internal current. According to Larminie et al (2000), this crossover overpotential was correlated to the loss of approximately 1mA/cm² or equivalent to 0.03% of reactants supplied. This internal leakage was probably caused by slit between gasket and diffusion layer.

5.1.1.2. EFFECT OF FLOW FIELD TOPOLOGY ON CURRENT MAGNITUDE AND DISTRIBUTION

a. Effect of flow field topology on current magnitude

Table 5-2 presents magnitude of average current density, standard deviation, and their ratio for all flow fields when current was drawn at 0.6 Volt. This table also shows that for all cell voltage, average current density was increasing from Parallel, to 1-S, and to 3-S.

Table 5-2 Current density obtained for P, 1-S, and 3-S flow field (in mA/cm²)
operated at 350 sccm H₂ and 175 sccm O₂

Ch No	0.6 V			0.3 V			0.2 V		
	P	1-S	3-S	P	1-S	3-S	P	1-S	3-S
Average	25.538	31.004	46.965	61.283	76.377	119.952	75.247	93.359	146.622
Stdev	6.110	5.779	7.330	15.201	15.142	20.781	18.426	18.543	24.929
$\frac{Stdev}{Average}$	0.239	0.186	0.156	0.248	0.198	0.173	0.245	0.199	0.170

For parallel flow topology, when reactants reached inner surface of parallel flow field fixture, their flow split into three branches; two directions (x and y direction) in fixture plane driven by convection and the other (z direction) crossing gas diffusion layer to

catalyst layer. Since the resistance for convection at the flow field channel was smaller than that for diffusion through the porous carbon paper, the tendency of reactants to flow over the fixture surface was higher compared to that through GDL. This resulted in lower reactant pressure at electro-active area causing reduced current magnitude.

The other factor causing low current generation in P flow field is its tendency to flood. When water is produced and accumulated in certain part of gas diffusion layer, gas flow tends to keep away from this area and proceed through available alternative paths. This means that the gas has more 'options' to flow in order to avoid flow resistance. The consequence of this would lead to those areas which filled with water at early stage to become more flooded or even become dead spot producing low current. The evidence of this is given in the next sub-section describing flow field effect on the current distribution.

Serpentine (1-S) flow field has advantage over the parallel one as they have only single lateral path at the fixture surface thus giving higher thrust for reactants to reach the catalyst layer hence, providing higher reactant pressure for reaction. However, this one-line channel can introduce high drag force causing membrane drying.

The last design of flow field can be thought as the combination between simple-line serpentine and parallel topology. It has tortuous lines which consist of three parallel lines; each line is confined to around one third of the volumetric rate. The design helps to overcome drawbacks from the abovementioned two topologies. It provides sufficient pressure required to help better distribution of reactants over the gas diffusion layer. Compared to 1-S flow field, it has shorter reactant flow path from the inlet to the outlet

(approximately one third). As the path is shorter, friction and pressure drop will be lower. As the result, better humidity and reactant distribution can be achieved.

The relationship between the average cell current and the homogeneity can be established by re-examining data tabulated in Table 5-2. It can be seen that there is a reciprocal relationship between current magnitude and its standard deviation-to-average ratio. Parallel flow field, having the smallest averaged current density, exhibited the highest ratio while the opposite result applied to 3-S topology. Reason behind it is that homogeneous current distribution indicates higher utilization of electrocatalyst surface area meaning that more fuel and oxidant react at particular time leading to higher rate of electron generation.

b. Effect of flow field topology on current distribution pattern

⊕ Spatial distribution observed from parallel flow field

Current density distribution pattern for Parallel flow field were extracted and presented in Figure 5-3. The color scale applies in this contour map as well as that applies in Figure 5-4 and 5-5 is adjusted to include current density range generated by all three flow fields to facilitate clear comparison in terms of average performance magnitude and homogeneity. The points of the measurement are represented by intersection of the grid lines. Segment number is indicated near each intersection. Compared to later figures representing the performance 1-S and 3-S flow fields, figure below illustrates the relatively inhomogeneous condition occurred in parallel flow field. The color scale dominating this map is blue, which indicate the smallest performance average than other flow fields.

At segment 1 where the oxygen enters the cell, the performance was poor because of the effect of under-humidified gas inlet. As reaction at cathode proceeds, additional water is

generated to help local humidification of the membrane and ionomer sites. This results in better performance of subsequent segments. Lower part of the cell showed poor performance either as can be observed from Table 5-3. Row-averages of the segments located at the lower part of the cell (R3 and R4) were lower than the total cell average (25.54 mA/cm²). Since this experiment was running on oxygen, mass transfer limitation due to reduced oxygen partial pressure as it passes through the length of segment should impose small effect to cell performance. It looks like sign of flooding was observed despite high reactant flow rate involved. The reason for this reduced electrochemical activity here was likely due to accumulation of water at these lower segments of the cell.

Figure 5-3 Current Distribution of cell running on 350 sccm H₂ and 175 sccm O₂, 0.6 V, P flow field

This water accumulation occurred due to the fact that liquid form was favorable at low ambient temperature and as the gas flew through near inlet segments, it carried water produced at the prior segments. Hence its ability to remove water at subsequent segments decreased. The other factor was the direction of cathode flow which was parallel to gravity. Water produced at upper segments was brought into this zone by gas movement downward toward oxygen outlet. However, the major cause of this accumulation was the nature of parallel topology itself. As mentioned above, once a segment in P topology contains water

droplets within its gas diffusion layer, flow resistance in that area increases. Due to pressure distribution of parallel flow field, this area became a dead spot for the flow. Therefore, flooding was expected to occur there. These reasons result in improper water management at the bottom row of the cell. Hence, the resistance for oxygen diffusion to reach catalyst active sites near the bottom increases and current generation reduces.

Table 5-3 Average current density calculated for each row (i_r) in mA/cm²
operated at 350 sccm H₂ and 175 sccm O₂

Column Row	C1	C2	C3	C4	i_r
R1	17.71	34.00	30.56	31.14	28.35
R2	37.42	24.82	30.85	23.24	29.08
R3	19.74	27.30	19.32	26.60	23.28
R4	26.28	23.29	19.65	16.69	21.48
Average	25.54				

i_r = current density average from the segments within the same row

Water content at hydrogen inlet segment should also be low due to drying effect of high flow rate gas and electro-osmotic drag. This electro-osmotic drag was high due to the application of relatively high cell overpotential. However, performance of segment 13 was significantly higher compared to that of segment 1. This was likely because the segment was benefited from water generation at cathode which created differential in water concentration between cathode and anode. Consequently, this drove water back diffusion mechanism to increase proton conductivity at the anode side of segment 13.

✚ *Spatial distribution observed from 1-S flow field*

Experiment to study the effect of 1-S topology was done in the similar condition to that of parallel flow field. The profile of 1-S topology consists of lower current density obtained from the first four segments and higher current density obtained from the rest of the segments, as can be seen in Figure 5-4. Higher performance homogeneity compared to that

of Parallel Flow field can be evidenced from this figure. In addition, higher average current density is apparent as bright green color prevails in this figure.

Figure 5-4 Current Distribution of cell operated at 350 sccm H_2 and 175 sccm O_2 , 0.6 V, 1-S flow field

Topology of 1-S dictates the fuel and oxygen to flow in only one line over the inner surface of the fixture from the inlet to the outlet. This topology and high gas flow rate introduces under-saturated reactants in this experiment and causes higher drag force that tends to dehumidify the membrane. These factors give rise to reduced proton conductivity of the cell, especially for the segments near the inlet. As the reaction proceeds downstream, similar to that of parallel flow field, more water is produced. In addition to that, the subsequent segments are in contact with less dry fluid compared to the early (near inlet) ones.

On the other hand, combination of geometry-channel dimensions of 1-S topology with high flow rate facilitates higher pressure for reactants to overcome resistance through the gas diffusion layer. The pressure manifested in force is needed to reach electro-catalyst sites so that charge transfer reaction can occur in sufficient rate. The pressure also helps to move water product from reaction sites and to avoid it from accumulating, hence enables

uniform water distribution over the membrane and three phase boundary. Table 5-4 below evidences the lowest row of the cell which exhibits slightly higher performance compared to the overall average. The decrease of current density in R4 was probably due to under-humidified hydrogen entering the cell.

Table 5-4 Average current density calculated for each row (i_r) in mA/cm² operated at 350 sccm H₂ and 175 sccm O₂, 1-S flow field

Column Row	C1	C2	C3	C4	i_r
R1	22.34	21.41	24.73	21.41	22.48
R2	38.61	35.68	29.32	30.88	33.62
R3	36.36	36.03	35.89	36.60	36.22
R4	34.20	30.45	31.52	30.60	31.70
Average	31.00				

⊕ *Spatial distribution observed from 3-S flow field*

Current density profile for 3-S topology is quite different from those mentioned above due to the absence of drying zone near oxygen inlet as shown in Figure 5-5. Table 5-5 shows the performance of inlet row (segment 1 – 4) is even higher than the average of current density over the cell. Current generation was reduced in the middle part of cell and the value obtained seems to be relatively homogeneous over segments 5 to 16 with the exception of segment 14. This exhibits opposite trend from the 1-S flow field where lower performance was obtained at segments close to the oxygen inlet. Higher level of homogeneity compared to other flow fields can be seen clearly in this figure. In addition, the dominant color scale signifies the average current density is shifted to yellow, showing even higher level performance average than 1-S flow field.

At the inlet point, the volumetric rate regulated by this topology was divided into three convection paths. The division helped reactants distributed more uniformly over the

segment surface while maintaining sufficient reactant pressure. Compared to 1-S flow field, the proton conducting medium at the inlet point was less dry. Therefore, unlike other topology, the first row outperformed the other rows. This was the result of good balance between water content in the membrane and at the three phase boundary with gases flowing in.

Figure 5-5 Current Distribution of cell running on 350 sccm H₂ and 175 sccm O₂, 0.6 V, 3 – S flow field

Segment 13 and other segments in the lowest row where the hydrogen first approaching the cell, performed relatively poor compared to the averaged value. This is probably because of high reaction rate thus more water formation at upper part of the cell. Water brought by gas movement reduces gas pore so that reactants diffusion to active sites of reaction was impeded.

Table 5-5 Average current density calculated for each row (i_r) in mA/cm² operated at 350 sccm H₂ and 175 sccm O₂, 3-S flow field

Column Row	C1	C2	C3	C4	i_r
R1	48.56	54.66	57.34	55.93	54.12
R2	52.82	42.82	48.31	43.19	46.79
R3	47.60	48.30	45.95	44.05	46.48
R4	41.91	26.34	50.41	43.24	40.47
Average	46.97				

When discussing the pattern obtained by each flow topology, some segments showed unusual result compared to the other. Current density obtained from segment 14 of 3-S topology is an example. When the experiment was conducted at different setting, i.e. at 0.3 and 0.2 Volt or when the cell was rotated 180°, the response of this particular point was practically the same. These facts dismissed the possibility of water accumulation as a result of the location of segment 14 at the bottom of the cell. The cause for this anomalous behavior is possibly the defect in the MEA fabrication resulting in inhomogeneous catalyst distribution. This result reflects the challenge in producing MEA with homogenous surface active area (TPB) distribution.

5.1.2. Application of Electrochemical Impedance Spectroscopy to Segmented Fuel Cell

Based on the experience of previous study on the current measurement applied to segmented fuel cell, it was considered necessary to reduce the number of the segments. Understanding the experimental data from this sixteen-segment cell was relatively challenging, compounded by the lack of an appropriate model to simulate the effect of changes in operating parameters. Contact problem had some impact in the measurement, which had also been considered by other researchers' works as explained in Chapter 3. The reduction of the number of the segments to eight was meant to mitigate these difficulties. This reduction into 8 segments was achieved by connecting two adjacent segments in the same rows and the new segment numbering is shown in Figure 5-6.

Figure 5-6 Segment numbering for 8-segment mode

5.1.2.1 IDENTIFICATION OF GENERAL MECHANISM REPRESENTED BY IMPEDANCE SPECTRA OBTAINED BY USING SEGMENTED FUEL CELL AT DIFFERENT OPERATING POTENTIAL

At this stage, impedance reading was conducted prior to obtaining information for current distribution over the cell surface. Impedance spectra distribution as a function of operating potential was observed. The cell ran on 125 sccm hydrogen and oxygen, humidified at 25°C using single line-serpentine (1-S) flow field. The frequency range for the impedance test was 10 kHz – 0.1 Hz with 10 milli-volt (Root Mean Square) magnitude. Figure 5-7 shows the Nyquist diagram of segments' impedance spectra at OCV, 0.9 volt and 0.8 volt. The y-axis in this figure, as in other parts of the report, shows the negative value of the imaginary impedance component.

Figure 5-7 Impedance spectra at cell potential of (a) OCV, (b) 0.9V, and (c) 0.8V using 1-S flow field, 125 sccm hydrogen and oxygen.
Note the non-symmetry scale between Z_{Re} and Z_{im} axis for OCV and 0.9 Volt

For all segments, responses at these three operating potentials appeared to have three “patterns”. The term “pattern” was used here instead of arc and the explanation below will show the distinctiveness. Below the $-Z_{Re}$ axis (which means positive value of imaginary impedance component), impedance pattern at the highest frequency part (2.5 kHz – 10 kHz) appeared as inductance dominates the cell response in this frequency range. This pattern can also be called as arc since this pattern only represents one mechanism. The inductance response is mostly due to wire connection and instrument impedance. Since this response exists due to external measurement setup, little attention will be given to this mechanism.

The second visible pattern of the spectra began from the intercept of the arc with Z_{Re} axis. As can be observed from Figure 5-7, each segment intersects the axis of real impedance at different values showing the variability in the segmental performance (to be described later in this section). Starting from this interception, there was an appearance of linear-like impedance loci with frequency lower than that of inductance range (11 Hz – 2.5 kHz). Figure 5-8 shows the magnification of this part for segment 1 at OCV down to 0.7 Volt.

Figure 5-8 Magnification of high frequency (second) arc of segment 1 from OCV to 0.7V

The second part of the spectra appeared to show linear characteristic and the angle formed by these curves with Real Impedance axis (θ) was nearly 45° or $\pi/4$. There are two known mechanisms which give similar response ; (1) finite diffusion of reactant from the bulk gas to approach electrode surface in solid state system, known as Nernst impedance (Bonded Warburg diffusion) or (2) Porous Electrode system with purely capacitive walls at high frequency, which can be represented by Transmission Line model (Macdonald, 2005). By considering that at this low overpotential the diffusion limitation is insignificant, the second mechanism appeared to be the nearest explanation for this response. One supporting fact is that this first pattern of the conductive arc was a weak function of cathode potential, at least for this wide potential range under study, which differ the double layer charging process from the diffusion ones.

In general, the magnitude of the angle obtained for each segment at all potentials was smaller than 45° . The difference was because of, in the Porous Electrode System Model, the pore was assumed to be cylindrical pore distributed uniformly on the electrode surface. The cells used in this experiment, and in fact applied to all fuel cell electrodes in general, had significant variation in sizes and dimensions of the catalyst pores at the electrode surface. In addition, the use of solid electrolyte in the electrode imparted additional influence on this. This result obtained is in agreement with the work of Paganin *et al.* (1998).

The last pattern of impedance spectra for OCV showed a nearly linear plot at lower frequency range. This appearance can be attributed to be the beginning of semi circle with large Charge Transfer Resistance. At 0.9 volt and 0.8 volt, this resistance decreased and, as

a result, a more curve-like plot emerged. Simple simulation showing the effect of Charge Transfer or Parallel Resistance to the impedance loci is shown Appendix C. It can be seen from Figure 5-7 and 5-9 that, as the cell potential decreased, the magnitude of this last pattern decreased as well. It is worth to note that the second and the third patterns belonged to the same arc family whose response, due to the distributed pore properties instead of uniform ones, showed linear response at higher frequency and slightly distorted capacitive curve at lower frequency (Real *et al*, 1993). This arc represents the Faradaic reaction occurred at the surface active area of the catalyst.

Figure 5-9 showed the impedance response of the cell at operating potential of 0.7, 0.6, and 0.5 Volt. Compared to the performance illustrated in Figure 5-7, in general, the decrease of Charge Transfer Resistance (the arc diameter) is more pronounced in lower cell potential due to exponential relationship between overpotential and current generated, as expressed in Butler-Volmer equation. Therefore, the size of the low frequency semi circles here is significantly smaller compared to that of the previous figure. As mentioned previously, similar second pattern of impedance response appeared in the same frequency range, supporting the explanation that this mechanism was due to the contribution of capacitive behavior of porous electrode.

Similar to the result presented in Figure 5-7, most responses for cell potential 0.6 and 0.5 Volt showed only one arc response. However, the responses of segment 1 and 8 at 0.5 Volt appeared to have an additional arc at lower frequency arc which seems to be diffusional related. Further explanation in Section 5.1.2.4 dismisses this likelihood.

Figure 5-9 Impedance spectra at cell potential of (a) 0.7 V, (b) 0.6 V, and (c) 0.5 V using 1-S flow field, 125 sccm hydrogen and oxygen

Explanation above showed that for the potential range under study, the mechanisms occur at each cell potential of this 16 cm² MEA were similar for all segments. These mechanisms involved the inductive arc of measurement setup and capacitive Faradaic reaction occurred at non uniform electrode surface. Another common capacitive arc, i.e. the diffusion arc, was not appeared within this range. However, thin film-agglomerate model reveals that response that displays only a single arc may contain not only Faradaic process resistance but also diffusion factor. Only the second mechanism will be considered further since inductance mechanism was controlled by external factor. In order to understand the dependence of this Faradaic reaction mechanism represented by high frequency capacitive arc, analogue approach was then conducted to quantify the transfer function parameters.

5.1.2.2 ANALOGUE APPROACH: THE EFFECT OF CELL POTENTIAL ON THE ARC PARAMETERS

Ideally, one arc response of such shown in Figure 5-7 and 5-9 should be fitted against an equivalent circuit which takes into account the porous electrode behavior represented by transmission line (TL) model. Building such equivalent circuit is difficult and also not within the scope of this study. Therefore, in order to approach this problem, initially impedance data was fitted against equivalent circuits consisted of one R-CPE arc arranged in series with electrolyte resistance. Constant Phase Element (CPE) was used here to simplify the TL model in representing the actual distributed time constants (thus parameters) due to the porous and inhomogeneous nature of electrode surface. However, it was later found out that one arc fitting could not work well for the result obtained at OCV and 0.9 volt, due to the presence of the line with an angle close to 45° as mentioned before, but it works with rather low statistical match (chi-square value of fitting) for other operating potentials.

In light of all concerns, despite the fact that the spectra represented only one mechanism, the data was then fitted against the equivalent circuit consisted of two arcs as illustrated in Figure 5-10. Parameters obtained from this equivalent circuit would be HFR for the electrolyte resistance and two sets of arc parameters (Parallel resistance – R_p and Constant Phase Element parameter – T and n , the exponential term). In this case, the R_{ct} was obtained by summing $R_{p,1}$ and $R_{p,2}$. Simple simulation was carried out to confirm that this method was reasonable to obtain the high accuracy for R_{ct} . In general, index 1 was assigned to the properties of higher frequency arc (arc of smaller time constant) while index 2 assigned to lower frequency arc. R_p notation for the pattern (half-arc) diameter is used to avoid confusion with the total arc diameter (R_{ct}) representing one mechanism. In

later section, $R_{ct,1}$ is attributed to the Faradaic resistance while the $R_{ct,2}$ is attributed to the hindrance for diffusion mechanism.

Figure 5-10 Two arc equivalent circuit for the fitting of the segments response

The complete fitting result is given in Appendix D. The statistical analysis given in Table 5-6 was done to understand the effect of the cell potential on the fitting parameters. In this table, average value for each parameter was calculated for a particular potential. Next, the standard deviation and parameter averaged over the whole potential range were evaluated to obtain the standard deviation/average ratio. This ratio showed the homogeneity of parameters over the selected voltage and how much this parameter was affected by the cell voltage. The higher the ratio means the more dependent of this parameter on the applied potential.

The properties of Constant Phase Element (T and n) showing the characteristic of surface active area as well as three phase boundary were relatively unaffected for potentials above 0.7 volt, especially the values of n . These values show that in general, the phase angle of the half arcs (patterns) remain constant, hence the surface condition. The trend starts to change at 0.7 volt possibly because of water begins to accumulate and change the morphology of the surface active area.

Table 5-6 Calculation of Standard Deviation/Average ratio to study the effect of cell potential to model parameters

Average¹⁾ Potential	HFR	R_{ct}	T₁	n₁	T₂	n₂
OCV	0.092	29.870	1.236	0.556	0.743	0.969
0.9 Volt	0.091	10.772	1.255	0.556	0.770	0.973
0.8 Volt	0.089	0.492	1.515	0.538	1.121	0.996
0.7 Volt	0.089	0.124	0.864	0.643	1.024	0.933
0.6 Volt	0.088	0.079	0.793	0.690	1.150	0.905
0.5 Volt	0.092	0.059	0.485	0.811	1.096	0.806
Average ²⁾	0.090	6.899	1.025	0.632	0.984	0.930
StDev	0.002	12.024	0.376	0.106	0.181	0.069
StDev/Avg	0.018	1.743	0.367	0.167	0.184	0.074

Note: 1) is the average value of the parameter for particular cell potential

2) is the average value of the parameter over the cell potential range

As far as surface morphology is concerned, it is known that the response of a smooth planar surface is similar to that of capacitor under the perturbation of ac signal, which corresponds to CPE with n value = 1. It can be seen in the table above, the value of n₁ was relatively far from the value 1 while n₂ behaves otherwise. This information revealed the characteristic of a porous system. At high frequency where the penetration depth of perturbing ac current is low resulting in semi-infinite manner of pore response and phase angle around 45°. As the frequency goes lower, penetration depth of the signal at low frequency increases and the pores are ‘unfold’, so that the response changes towards the characteristics of capacitor.

The standard deviation to average ratio for HFR is the smallest among the parameters of interest, proving that the change in cell potential imposes slight effect on HFR within this range. Figure 5-11 presents the value of HFR extracted from the above experimental data. It is clearly observable that the HFR values of each segment change very slightly for cell potentials from OCV to 0.5 Volt.

Figure 5-11 HFR distribution for 8-segment cell, running on 1-S topology, 125 sccm H₂ and O₂

Section 2.1.4 explained that cell resistance related to the transport of charged material thus causing ohmic loss is independent of cell potential. However, it is also explained that the major part of this resistance comes from the limitation due to low proton conductivity (HFR), which is water related issue. Hence, it is interesting to learn that despite the higher extent of water generation at lower cell potential, the HFR of each segment has remained unchanged. There is possibility that the extent of electrochemical reaction took place at the segments' TPB caused very small change in membrane moisture level. Therefore, it is necessary to take into account the Charge Transfer Resistance in order to understand this result better.

The R_{ct} showed the highest sensitivity to change in operating potential as expressed by the Butler-Volmer equation in Chapter 2 (equation 2-2). Combining this information with the outcome of HFR fitting, it appeared that the amount of water generated from the reaction increased the humidity of the Three Phase Boundary. If mass balance were examined carefully, the fuel utilization in this experiment was less than 10% and thus water generated from the reaction would be accordingly small to affect the water content of the

membrane retained in the cell pre-treatment step. However, this amount of water has significant impact on the water content of Nafion phase at Three Phase Boundary since the volume of this phase was very small compared to the volume of the membrane. Another significant factor was the distance for diffusion. Water generated from reaction could readily humidify the electrolyte (Nafion) of the TPB the since this electrolyte was right surrounding the catalyst site. Thus, there is no significant barrier for water diffusion and uptake in the electrode. On the other hand, water from reaction would need to overcome diffusion barrier to reach the membrane.

Description above reveals that the locally resolved impedance measurement was very useful to obtain probable mechanisms occur at different segments of the fuel cell. Statistical manipulation provided by analogue/equivalent circuit fitting approach revealed that different cell parameter has different dependency on cell potential. The study presented in the next section attempts to correlate the segments' current with impedance response to analyze the magnitude and variation of the segment performance.

5.1.2.3 PERFORMANCE VARIABILITY OVER THE FUEL CELL ELECTRODE AREA

As explained in the sections above, all segments experienced the same mechanisms when tested under potentiostatic mode in the range of OCV – 0.5 Volt. However, observation on segments' spectra revealed that the extent of these mechanisms varied among the eight segments. In addition, it can be seen that the absolute value of each segments' current density shown in Figure 5-12 increases as the cell potential decreases. This means that the trend exhibited at OCV was similar to that exhibited at 0.5 Volt but with different in magnitude of the parameters.

Figure 5-12 Polarization curve for 8 segments running on 125 H₂ and O₂, 1-S flow field

One noticeable feature observed from the whole impedance dataset was that the rank of the segments' responses was relatively constant for different cell potentials. Inspection on Figure 5-7 and 5-9 above disclosed that segments located at the top and the bottom row (S1, S2, S7, and S8) had smaller resistance compared to the middle ones (S3, S4, S5, and S6). Polarization curve above also gave similar pattern except for segments 1 and 2 at cell potential below 0.4 volt. The patterns of High Frequency Resistance and Charge Transfer Resistance were investigated to understand further the trend.

As explained above, the HFR value of each segment has remained unchanged when the cell potential was reduced. Consequently, the HFR distribution pattern also remains the same. One interesting information to note is that, even though the HFR was unaffected by the cell potential, the distribution pattern of this parameter over the segments was mirror to the segments performance pattern. Figure 5-13 shows that the HFR pattern is inversely

proportional to the current density pattern. It can be seen that the segment located in the center had high HFR is accompanied by low current density. Since the trend of the current density was constant for all cell potentials, this correlation is applicable to this set of experiment. This trend was in good agreement with other sets of experimental results using 3-S flow field and the results obtained by Cleghorn *et al.* (1998).

Figure 5-13 Current density and High Frequency Resistance obtained at 0.6 Volt

The distribution of R_{ct} at different cell potential is displayed in Figure 5-14 below. This resistance has relatively similar trend with HFR even though its correlation with current density was not as precise as HFR. In general the pattern reveals that the middle segments have higher R_{ct} value than the peripheral ones, especially at low cell potentials. The trend shown by these resistances explains the variability in current density trend; the higher the value of these resistances, the lower the current output will be.

It is also clear that performance wise, the segments could indeed be divided into two groups as indicated above. Segment 1, 2, 7, and 8 belonged to the group with low HFR and R_{ct} , hence experiencing high current density. The other segments can be categorized as the second group behave otherwise, especially segment 4 and 6. With reference to segment

numbering scheme used in Figure 5-6, the first group was located at the top and the bottom of the row (peripheral position) while the second group was located in the middle of the cell.

Figure 5-14 R_{ct} distribution for 8-segment cell at different cell potential, running on 1-S topology, 125 sccm H_2 and O_2

The configuration selected positioned the oxygen inlet at the top row (segment 1) and the hydrogen at the bottom row (segment 7). The first group was benefited from its location close to the inlet of hydrogen or oxygen as humidified reactants entering the cell helped maintaining water level of these rows. Therefore, as the proton conductivity increases, the performance would eventually improve. In addition, the 1-S topology used in this experiment facilitates high thrust for reactant streams to reach their outlets but the higher

reactant pressure would be at points close to the inlets. It is known that higher reactant partial pressure would lead to higher electrochemical reactions hence more water production. Segments 3 and 5 located in the same segment column as both reactants' inlets, hence even though they were located in the middle rows, they could still obtain the inlet humidification effect as well as higher reactant concentration as the topology of 1-S also facilitates high thrust for reactant lateral diffusion in the Gas Diffusion Layer (GDL). This effect was not available to segments 4 and 6 which are located far away from the reactant inlets.

In addition to the factors above, the position of the first group at the peripheral of the cell caused the segments closer to the bracing bolts where the torque was applied, resulting in higher contact pressure. Therefore, allowing smaller contact resistance among the segments' components. Qualitative verification using pressure sensitive film displayed in Figure 5-15 shows that segments of the first group produce higher color intensity indicating better contact pressure. It is shown in Figure 5-12 that segment 6 exhibited very low current response for all observed potentials. The possibility of high contact resistance was noted and will be discussed further in Section 5.1.2.4.

The study presented so far in this chapter has shown the usefulness of segmented fuel cell in acquiring information on the performance distribution over the geometric surface area of the PEMFC. It also can be seen that the application of Electrochemical Impedance Spectroscopy in segmented fuel cell in addition to widely used current measurement method provided useful data in identifying key factors determining the cell performance or

degrading it. Nevertheless, there are few things need to be considered in order to increase the accuracy of the measurement, as discussed in Section 5.1.2.4 below.

Figure 5-15 Qualitative verification for contact pressure of eight segments using pressure sensitive film

5.1.2.4 DATA ACQUISITION ASPECT IN SEGMENTED FUEL CELL APPROACH

This section addresses some technical challenges encountered during data acquisition process in order to improve the quality of measurement using segmented fuel cell. These issues include:

a. Poor segment response

Segment 6 demonstrated very low current generation indicated by vertical-like polarization curve in Figure 5-12. Magnification of polarization curve obtained from this segment is shown in Figure 5-16. The current density registered increased with the decrease of cell potential and consistently followed the performance rank as the smallest but the value was very low, around 100 times smaller than the next segment in rank (segment 4). This result is difficult to justify since, even though on average this segment exhibits the highest HFR and R_{ct} , the EIS spectra for this segment seems normal. However, at 0.5 Volt, this segment exhibits unusual response so the whole response appears to be lifted up from the real

impedance axis. It is worth to recall that polarization curve registration was done after impedance spectra were collected. Further investigation is needed to understand the nature of this behavior.

Despite the last impedance result, further examination on active area of MEA after the test and contact pressure test did not reveal any abnormalities explaining this result. When the test was conducted using automated electromagnetic switch from Solartron 1470E, the same symptom was shown on other segments as well, preventing the use of this multipotentiostat for the time being. Contact resistance problem occurred under loading condition is possibly the cause of this problem. More investigation including the use of different configuration and fixture base material is proposed to probe this issue.

Figure 5-16 Magnification of polarization curve registered from segment 6

b. Measurement time and switching method

One characteristic of measurement using sequential switching is that current measured for one segment is actually the total current generated from the active area of the electrodes but gathered at the point where the probe was located. Therefore, the participation of the neighboring segments is included but the dominant part of this response comes from this particular segment. The use of simultaneous measurement to probe all the segments at the

same time helps to reduce the participation of other segments' current by creating more paths for current to flow.

Another feature of the sequential multiplexing is the measurement time, which depends on the number of segments, i.e., the more the segments the longer the time required for one measurement cycle will be. Capacitive current response will appear as the testing device begins drawing the current prior to Faradaic current response under investigation. Therefore, certain amount of time is required to allow the exponential response of the capacitive current to disappear so that equal initial point for the study of Faradaic process can be obtained. This causes longer time to obtain useful data set. Therefore, manual switching is applicable only to observe the quasi steady state performance, as performed in this section.

Even though fast response to load change is one of the characteristic of PEM fuel cell, the distribution and performance of the cell can change when water condensation occur at the three phase boundary or, in the worst case, flooding. It is known that the performance of the active area will deteriorate when this happens. Depending on the electrode and bipolar plate's design, the accumulated water can be removed from the catalytic area by flushing mechanism due to the porous nature of the electrodes. The mechanism of flooding and water removal through flushing as a function of time are not yet fully understood, probably due to difficulties lie in the complex interrelationship among operating parameters and design factors. Hence, the occurrence time could not be estimated accurately and it would be difficult for manual switching method to be applied to capture the entire time history of these processes. However, response of segments 1 and 8 in Section 5.1.2.1 shown in Figure

5-9 gives the sign of water condensation and can be explained later in point c (2) below. Since flooding and water management are keys to the performance of low temperature fuel cell, understanding the mechanisms of these processes are essential. It is hopeful that the use of simultaneous or near real time multiplexing sampling technique can help in identifying these “symptoms”.

c. Complexity in data interpretation

(1) Selection of mechanism to certain dataset

One of the strengths of the Impedance Spectroscopy is that it retrieves the system information at power source terminals allowing observation of all dominant mechanisms at a given set of cell operating conditions. This technique is suitable for PEM fuel cell where the insertion of any sensors into MEA will (significantly) disturb normal processes especially due to its small dimensions. On the other hand, the impedance acquisition at source terminals also means that the spectra obtained are not specific for certain mechanism or element. In addition, EIS is not similar to any direct measurement (*e.g.* temperature or pressure) where data acquired can readily be understood physically. Thus, equivalent circuit reflecting the actual processes involved is required to extract information from the cell responses. This equivalent circuit builds analogies between the response of the system under investigation and a set of electrical as well as electrochemical elements whose behavior toward the application of ac signal are known. These analogies are then used as patterns or model for identification of mechanisms occurring within the system. However, it is known that the selection of this equivalent circuit is often challenging since certain dataset can be represented by more than one circuit with equivalent statistical match.

Another difficulty arises when the cell response is not ‘standard’ as exemplified by cell response in Section 5.1.2.1. In this case, the impedance arc having nearly 45° line at high frequency could represent two different mechanisms: porous system response or Nernst diffusion, which is often overlooked in discussion of PEM fuel cell response. It appeared that lack of discussion on non standard mechanism in PEM Fuel Cell is due to limited mechanisms library available for PEM fuel cell. In addition, in above case it was difficult to tell which key performance factor occurred by just looking at the sole available impedance spectra without other supplementary information on cell potential and nature of the solid-solid system. Fitting of equivalent circuit would be useful to get the system parameters but pattern recognition based on prior knowledge of the system and the impact of operating condition is of high importance in interpreting impedance spectra correctly.

Since each cell will likely give different response due to differences in cell design, MEA fabrication, material used, etc., building the fuel cell mechanism library can speed up the process for performance and degradation identification.

(2) Intermediate Response

The responses of segment 1 and 8 at 0.5 Volt shown in Figure 5-9 (recaptured in Figure 5-17 (a)) showed interesting feature since they seemed to have additional arc in the low frequency region. In order to understand this phenomenon, examples of impedance spectra obtained from other experiments were studied and compared to those obtained from segment 1 and 8. The spectra showed in Figure 5-17 (b) was registered from unsegmented fixture to observe the effect of initial humidification temperature on the cell response. The experiment was conducted at 0.6 Volt using 1-S flow field, 84 sccm H₂ – 42 sccm O₂. The

response was taken while the temperature of cathode humidification chamber was raised to 60°C without anode humidification. Different from that presented later in Section 5-3, in this (b) case the humidifier temperature was still at room temperature when the current loading began and then it increased to reach humidification temperature. Therefore, the development of the second arc towards higher moisture level was clearly shown.

Figure 5-17 Second arc-like feature observed during measurement from response of
 (a) segment 1 and 8 of 1-S topology segmented fuel cell, 125 sccm H₂ and O₂
 (b) 1-S unsegmented fuel cell, 84 sccm H₂ and 42 sccm O₂, as the cathode humidification chamber temperature was heated up to 60°C, no humidification at anode

The six impedance loci in Figure 5-17 (b) were obtained at different time. The first cluster consists of impedance spectra taken consecutively at 18th, 22th, and 26th minute. The characteristics of response at 22th minute (the middle response for cluster I) appeared to be

similar to that of segment 1 and 8's response. The data of second cluster were taken at 94th, 98th, and 102th minute. For each cluster, the middle spectra had high frequency response similar to spectra registered previously but part of the low frequency response resembled to that registered subsequently. These spectra are rarely discussed in the work related to fuel cell.

Confusion frequently arises when dealing with this kind of response due to the missing of trend continuity compared to the next measurement. For segmented fuel cell with manual multiplexing, this type of responses appears anomalous when compared to the sub sequential spectra obtained from the same segment or to that from the neighboring segments. In addition, data interpretation for both clusters can be incorrect and lead to different conclusions. For the first cluster, the jump occurred at the lowest frequency range seems insignificant. Hence, the impedance loci at this frequency tail are often discarded since it reduces the fitting accuracy. It is also possible that the data is being ignored since it was thought to be an error of the measurement. On the other hand, the notable jump in the second cluster could be mistakenly taken to have additional arc indicating the occurrence of different process. However, despite the lack of prior information for this type of responses, these spectra could provide useful information to facilitate performance degradation identification.

The results of current measurement conducted right before each impedance test in experiment (b) is presented in Figure 5-18. It reveals that there was a change in current level at around the time when the middle spectra of each cluster was taken. It is clear that as the middle spectrum for each cluster jumped to a bigger arc diameter, the current

generated from the cell was reduced. Again, by using prior knowledge of the fuel cell fundamental and pattern recognition, it could be concluded that the increase in water condensation happened at that particular time.

Figure 5-18 Current as a function of time at 64 sccm H₂ and 42 sccm O₂, as the cathode humidification chamber was heated up to 60°C, no humidification at anode

Later in this project, it was found that this kind of sudden change was often recorded as the cell response was registered along time. It can be seen that this type of information is useful to identify the progress of mechanisms as it contains the measurement history. These spectra also offer the possibility in exploring transient phenomena and time scale in fault development.

5.2. Thin Layer-Agglomerate Model Approach to Analyze the Performance of PEM Fuel Cell

In this set of experiments, the data obtained from current measurement and impedance spectroscopy were studied to observe the difference between performance of cells running on oxygen and air. Unsegmented/total fuel cell with MEA of 7.5 cm^2 was used. Hydrogen flow rate was adjusted to stoichiometric ratio (SR) = 1 (60 sccm) while the oxygen flow rate to SR = 1.5 (45 sccm). The corresponding flow rate for air was 205 sccm. Both reactants were humidified prior to entering the cell at humidification temperature of 25°C . Figure 5-19 below shows the polarization curve obtained from current measurement of these two cells. Data is obtained by maintaining the cell at certain potential for 5 minutes for current registration (potentiostatic-step mode). The step potential is 40 mV.

The figure demonstrated that the cell running on air has lower performance compared to the cell running on oxygen. At 0.6 Volt, current density of the oxygen cell was 93 mA/cm^2 while the air cell gave 62 mA/cm^2 . Even though the same amount of oxygen was supplied to the cell within the same periods of time, oxygen partial pressure of air is only 21% of that of pure oxygen partial pressure since gas partial pressure is proportional to the gas fraction (X_{O_2}); $P_{\text{O}_2} \sim X_{\text{O}_2} \times P_{\text{Total}}$.

This lower partial pressure led to lower open circuit value, which is the highest available potential value for electron generation. This OCV can be used as a mean of prediction that the higher the OCV, i.e. the bigger the portion of overpotential can be used for the current generation reaction. On the other hand, theoretical prediction proposed by Nernst (equation 2-1) showed that the difference in oxygen content between pure oxygen and air would

result in only 10-mV difference in open circuit potential, as the partial pressure is in natural logarithmic term. The data obtained in the experiment was close to the prediction: the OCV obtained from the oxygen cell reached 0.93 Volt at the beginning of the reaction versus 0.9 Volt of the counterpart.

Figure 5-19 Polarization curve for the cell running on oxygen and air, $SR_{H_2} = 1$ and $SR_{O_2} = 1.5$

It was also observed that when electrons began to flow from anode to cathode, the difference among the current densities was more pronounced. As the overpotential increased, the difference between the air cell performance and the oxygen one became more prominent. The reason for this was the introduction of nitrogen as non-reacting inert gas which is four times the volume of oxygen in air. Its dominant availability in the oxidant stream affected the mass transport at the cathode side by impeding oxygen diffusion from bulk gas into the catalyst layer, which in turn would reduce oxygen supply rate to the reaction sites. As a result, oxygen concentration at the surface active area was lower. Since the reaction rate is proportionally related to the reactant concentration at the catalyst surface as shown in equation 5-2 below, lower oxygen partial pressure in air is

directly related to lower reactant concentration/partial pressure at the TPB which leads to slower reaction kinetics.

$$i = F A k [O]_o \quad [5-2]$$

In this equation, i is the rate of electron generation which is known better as current, F is the Faraday constant, A shows the surface active area of the catalyst available for reaction, k is the rate constant, and $[O]_o$ is the reactant concentration at the three-phase boundary. As the overpotential increased, the required oxygen supply rate increased as well.

One interesting point to note from Figure 5-19 is that the polarization curve for the cell running on oxygen and air showed relatively similar pattern. Both curves showed activation and ohmic losses. It was expected that diffusion polarization would occur especially at higher overpotential for the air cell since this appeared to be dominant factor causing performance degradation for this cell. However, no sign of diffusion limitation appeared in the curve. In addition, impedance spectra collected for both cells mostly had one arc and did not reveal the diffusion mechanism. Figure 5-20 illustrates some of the spectra samples for air and oxygen cell. From mechanism identification point of view, this suggested that another approach would be needed to reveal and isolate this fault. Thin Film-Agglomerate model was then used to distinguish the performance of these two cells. In this model, calculation was made based on the polarization curve above with EIS reading to reveal different mechanisms leading to the performance limitation in air cell.

The impedance spectra was collected for both oxygen and air cell at the same cell potential as in the current measurement method. Time constant variation was found in both data sets but not as clear as that found in segmented fuel cell. This is probably due to smaller MEA

size and lower catalyst loading used in this experiment (0.6 mg/cm^2) compared to the one used in segmented fuel cell (1 mg/cm^2). This lower loading led to less packed and smoother interface. Hence, MEA used in this experiment demonstrated responses of less porous and more homogeneous electrode surface. Nevertheless, equivalent circuit of two semicircular arcs (R-CPE) in series with HFR, which is same as that illustrated in Figure 5-10, was still used to fit the data in order to achieve higher accuracy. In this section, Total Parallel Resistance (R_t) is used instead of R_{ct} to represent the arc diameter. This is because one of the purposes in Thin Film-Agglomerate model is to identify the diffusion occurs in agglomerate region which is often masked by the response of the Faradaic reaction resulting in one arc response only at high frequency loci. One indication for this condition is that the cell shows one arc response for a relatively broad potential range. The complete fitting result is tabulated in Appendix E.

(a)

(b)

Figure 5-20 Samples of impedance spectra at different cell potential showing one arc characteristic from (a) oxygen cell (b) air cell

Similar to the previous case, the fitting result showed that there was apparently negligible change in membrane conductivity for these measurements due to relatively constant/saturated water content after the cell went through activation step. It was also apparent that as the cell potential decreased, the diameter of the arc reduced accordingly and in faster rate. In order to examine the result further, the arc diameter, R_t was extracted from the fitting result. Figure 5-21 below is obtained by plotting the cathode potential against the logarithmic value of reciprocal of R_t . The iR -correction was performed to exclude the ohmic losses in cell potential leaving cathode potential part for the plotting. In this calculation, the main losses in the cell were assumed to occur at cathode.

Figure 5-21 demonstrates the usefulness of Thin Film Agglomerate to separate different processes occurred within the cell. This method was capable of differentiating various regions which were inseparable by using current measurement method and EIS. The curve presenting the plot of $\log (R_t^{-1})$ vs. cathode potential for oxygen cell in part (a) showed three different slopes corresponded to three distinct regions. These slopes changed from lower negative value to higher ones, representing alteration of mechanisms as the cathode potential decreased. The slope of the first region indicated electrochemical reaction at the cathode active area as the determining step at this high potential range. In this region, reduction in arc diameter was purely controlled by kinetics mechanism as can be explained by using Butler-Volmer equation given in equation 2-2. The equation described the correlation between current generated as a result of catalyst activity and overpotential applied to the cell. Recalling this equation with elimination of the second term due to considerably large value of overpotential gives:

$$i = i_o \left[\frac{C_R^*}{C_R^{0*}} \exp\left(\frac{\alpha n F \eta}{RT}\right) \right]$$

The decrease in cell potential through potentiostatic device control corresponding to the increase of overpotential to drive electrochemical reaction. Following the definition of impedance in equation 2-19, it is clear that the linear decrease in cell potential (i.e. the increase in overpotential) would lead to fast reduction in impedance as the current increases exponentially.

Figure 5-21 Plot of V_{cell} vs $\log R_t^{-1}$ for (a) oxygen cell (b) air cell

In the middle cathode potential range, the absolute value of the curve gradient suddenly increased, around four times the value of the first slope. The change in gradient magnitude

could be associated with progressive depletion of oxygen at the cathode agglomerate region though diffusion limitation has not developed in the thin layer. In mathematical term, the abovementioned condition was correlated to the nonzero value for the agglomerate diffusion parameter (Φ). On the other hand, the parameter describing the thin film diffusion (Γ) remained zero. This change can also be interpreted as the beginning of diffusion limitation, caused by the increase in supply requirement due to faster reactant conversion at the cathode TPB. Current measurement method as well as EIS was incapable of capturing this phenomenon. Further observation on impedance spectra at this potential range would show slower decrease in arc size with the same decrease in cathode potential. However, this observation tended to be inaccurate.

Starting from cathode potential of 0.51 Volt (the lowest cathode potential range), the third slope appeared in the oxygen cell as the consequence of non-negligible thin film diffusion limitation in the electrolyte layer surrounding the agglomerate region. This means nonzero value for both agglomerate and thin film diffusion parameter. Additional diffusion resistance resulted in even slower decrease rate in the arc size compared to the middle potential range. As the rate of electron generation increased, more oxygen was required while at the same time water accumulation impedes oxygen transport.

The values of these slopes were tabulated in Table 5-7 along with those for the air cell counterpart. Mathematical derivation given in Chapter 3 explained that the first slope should be close to Tafel slope or $b = 2.3 \frac{RT}{\alpha nF} \sim 120 \text{ mV/decade}$ for $T = 298^\circ\text{C}$ and $\alpha = 0.5$.

The slope obtained in this experiment was twice of the b value above, which was also close to the value obtained for ORR in liquid electrolytes. Furthermore, comparing the result to

the work done by Ciureanu *et al.* (2001), it can be seen that the slopes obtained at this experiment (for s1 and s2) were twice or three times of their results. Their impedance spectra showed almost no feature of porous electrode response. Raistrick (1990) noted that in the presence of distributed electrolyte phase resistance within the pore, the slope could reach value as high as 4b. From this explanation it appeared that the doubling value at the highest cathode potential was because of the non uniform nature of the electrode resistance.

Table 5-7 Slopes obtained from for oxygen and air cell at 25°C
60 sccm H₂ and 42 sccm O₂ / 201sccm air

Slope (V/decade)	Region 1	Region 2	Region 3	Region 4
Oxygen	-0.2201	-0.7972	-3.6323	-
Air	-0.2778	-0.7814	-5.5042	2.6338

It can be seen that the first three slopes found in the plot of the oxygen cell were also found in the performance of the air cell. The value of slopes 1 and 2 of both cells were comparably similar but the absolute value of the last slope for air cell was significantly higher than that of oxygen cell. Difference in the extent of diffusion limitation at thin film region due to the presence of nitrogen in air was possibly the cause of this difference.

Another interesting feature obtained from this approach was the presence of the fourth slope in plot 5-21 (b) that distinguished the response of the air cell from the oxygen counterpart. The last gradient, different from the others, has positive slope began from cell potential of 0.5 Volt. In the sets of spectra illustrated in Figure 5-22, it can be seen that starting from this potential, the arc diameter or R_t did not decrease anymore as the cathode potential decreases. By considering low potential condition, it appeared that the gas diffusion backing next to the electrolyte layers was on the onset of flooding. As the result,

oxygen replenishment was slower than needed to supply the ORR and diffusion mechanism began to control the polarization behavior of the cell.

Figure 5-22 Impedance spectra obtained at 60 sccm H_2 and 201 sccm air, 25°C showing increase of R_t at cathode potential below 0.5 Volt

Explanation above demonstrated the capabilities of the Thin Film-Agglomerate model in isolating the different cell processes which were difficult to probe using the conventional current and impedance data manipulation. This approach could clearly reveal the cause of performance losses in the air cell compared to the oxygen cell. Analysis given by this model had shown the effect of the presence of nitrogen in the cell reaction and diffusion.

5.3. Observation on Water Management-Related Factors Affecting the Performance of PEMFC

This last section focused on water management which is an essential factor for the performance of low temperature fuel cell. Water balance is an important issue since it is not only related to mass balance but also energy balance as reaction and phase change involved in it. Water transport within porous media due to concentration difference and ion transport complicate the identification of moisture level of the cell. In this series of experiment, several schemes to induce cell humidity were applied to the cell and spectra obtained were analyzed. In each experiment, cell performance was continuously registered within two hours in terms of current density and impedance under specific potentiostatic condition, 0.6 Volt. The choice of this time duration is to allow the observation of impact caused by the humidification scheme to take effect and the cell to reach steady state after the humidification is applied to the system. One cycle measurement last for four minutes with current measurement preceded the impedance assessment. Open Circuit Voltage was measured prior to the first measurement cycle. Similar to previous impedance assessment, perturbation signal of 10 miliVolt was applied within frequency range 10 kHz – 0.1 kHz.

5.3.1. Effect of Electrode Humidification on the Cell Performance

Figure 5-23 presents experiment results obtained from different humidification schemes applied to the cell. There are four curves in the figure, showing the performance of the cell when it ran at dry condition, cathode humidification, anode humidification, and both anode-cathode humidification. Dry condition here means that the reactants did not pass the humidifier chamber. Hence, the water content in the inlet was similar to the water content in the gas supply cylinder (<0.1%). The cell was set at ambient temperature. In humidified condition, reactants passed the humidifier chamber at 60°C.

Figure 5-23 Current density of the cell at (a) dry condition, (b) Cathode-only humidification, $T_{H,C} = 60^{\circ}\text{C}$, (c) Anode-only humidification $T_{H,A} = 60^{\circ}\text{C}$, and (d) Both Electrodes Humidification ($T_{H,A} = T_{H,C} = 60^{\circ}\text{C}$)

The cell ran without any humidification yielded in the lowest current density (118 mA/cm^2) with its magnitude was notably lower compared to other three conditions. Cell with cathode humidification was the next showing the low performance (142 mA/cm^2), followed by anode humidification (154 mA/cm^2), and both anode-cathode humidification gave the highest current density (157 mA/cm^2). The last humidification scheme also reached steady state current density in the shortest time. The performances from other three schemes advanced to reach certain current density at different periods and slowly increased from this point up to the end of measurement. There was indication that the currents would still increase beyond this two hours period. The corresponding impedance response is given in the Figure 5-24.

All data sets show the same tendency that HFR decreased fast at the beginning of data acquisition but slowed down and showed small change at the end of measurement. The cell operating in dry condition showed obvious gradual decrease in R_{ct} (indicated by arc

diameter) while the others appeared to reach steady R_{ct} in relatively short time, which is in agreement with current measurement presented in Figure 5-22.

Figure 5-24 EIS spectra obtained at different humidification schemes
The scale for dry inlet (top graphic) was different from the others due to its impedance magnitude

Unlike the result illustrated in the previous section about segmented fuel cell with manual multiplexing, HFR decreases as time lapsed. For both series of experiments, time imparts some effect to the cells condition and performance. In that previous testing, time influence in measurement result is due to the nature of manual multiplexing. The difference in this HFR behavior lied in the preparation step as explained in section 5.1.2. The performance measurement of the segments explained in the previous section was conducted after they had gone through an activation step for two hours. In this part, after the OCV measurement at the beginning of each experiment, no preparation/activation step was done.

At OCV, water transport to humidify the membrane was driven by diffusion which would be of very low rate. Since the cell did not exercise the activation step, the membrane remained rather dry in the beginning of experiment. As the load was applied and water generation reaction commenced, the reduction in HFR indicating the increase of membrane humidity was notable. On the other words, this information provides insight on the mechanism occurs during preparation step when certain operating condition and humidification scheme are applied to the cell. Therefore, this result supports prior explanation on the cause of constant HFR value of each segment in the absent of flooding when local performance measurement was conducted. This also emphasizes the need of preparation step for the cell to reach steady state, by applying load over a period of time, before the segments are assessed with manual multiplexing.

In no humidification scheme, water partial pressure of the reactants was negligible. At the beginning, the reaction at the cathode had not commenced yet and this practically provided very small amount of water for the electrolyte phase located at the three phase boundary,

resulting in slow proton transport. As Oxygen Reduction Reaction advanced, water is generated and diffused from the reaction sites to the surrounding electrolyte, which then sped up the reaction rate by improving proton mobility. Therefore, external humidity plays an important role at the beginning of the cell operation since practically no water was available within the cell. Due to its small amount in early period of experiment, water would take some time to stabilize its distribution within the proton conducting media. This explains why the cell in no-humidification scheme takes some time to reach its steady state.

In addition to increasing water content in the inlet gases, humidification allowed temperature of inlet reactants to increase when they came in contact with the heated water at the humidifier chamber. Sufficient insulation at inlet preserved the heat thus the additional energy contained within the reactants. This would increase the rate of electrode reactions. As discussed in Chapter 2, the activation energy decreased exponentially with temperature and higher reaction rate could be obtained. This difference in temperature made the performance difference between the humidified and non humidified schemes more pronounced.

The current density of cell with only-anode humidification was higher compared to the one with only-cathode humidification. As mentioned previously, proton conducting media at both anode and cathode Three Phase Boundary requires water to help transporting proton. However, as unique mechanisms take place, difference in electrode humidification had different impact on the cell performance. Simple calculation showed that the rate of water supplied from cathode reaction was at least several times higher than that supplied from external humidification. It was assumed in the calculation that fully humidified condition

could be reached which rarely occurs due to short contact time within the humidifier. In addition, hindrance for water diffusion to reach catalyst site, which can hardly be quantified, was not taken into account. Thus, it can be said that only small fraction of cathode humidification was brought by the inlet oxygen causing cell performance less sensitive to external humidification at the cathode.

On the other hand, the source for anode humidification comes from external humidification and back diffusion especially when water hydraulic pressure is high at the cathode. The back diffusion is prominent only at high current density. Since the experiments were performed at 0.6 Volt, water concentration at cathode was expected to be relatively mild. This assumption was supported by higher HFR value from cathode humidification scheme compared to anode humidification scheme at the end of experiment duration. This data implied that water back diffusion at this condition was not sufficient to replenish reduction of water amount at anode due to electro-osmotic drag. Thus the extent of water supply from external humidification was important. As the number of water molecules accompanying proton movement is important to enhance H^+ conductivity of membrane and is dependent on the amount of water available at anode side, the cell performance was highly affected by anode humidification.

The contact of both inlet gases with 60°C water in humidifier chamber introduced higher moisture content gases for the last experiment, resulted in the highest performance compared to other schemes. Water diffusion and distribution occur as humidified gases reached hydrophilic components of MEA improving ion conductivity resulting in faster electron generation. Temperature was another factor that helped both reaction and

diffusion. The effect of temperature on reaction has been mentioned above. On diffusion side, the rate of water movement within Nafion would be exponential with the increase of temperature.

Saturated condition was not obtained yet until the last part of this experiment. This is because the water removal via dispersing water molecules to the surrounding of cathode catalyst layer, in addition to evaporation, could occur effectively. As time lapsed, more water was accumulated at the cathode catalyst layer blocking oxygen from reaching the surface active area. This circumstance was revealed in the presence of the second low frequency arc at the end of measurement. Figure 5-25 enlarges the low frequency part of its response. Examination the current produced by both electrodes humidification on Figure 5-23 showed that there was slight performance decrease in current density at the end of assessment period. This trend was on the contrary to that observed from other schemes, where the current still increased after duration of two hours, showing non saturated state of the cells.

Figure 5-25 Low frequency response of cell with both electrodes humidified

Andreas *et al.* (2005) pointed out the possibility of assigning anode drying mechanism instead of cathode flooding as the cause for this second arc to occur. Cathode mechanism was chosen here based on the information shown in Figure 5-26. This figure enlarges the other end of spectra, which is the intercept of high frequency arc with real impedance axis, obtained for anode-cathode humidification scheme. The trend displayed in this figure is that HFR obtained in this experiment decreases as time increases. This indicates reduction in membrane resistance which only possible due to increase in electrolyte humidification. Drying mechanism would show otherwise.

Furthermore, considering that this experiment was set to draw medium current, it appeared that flooding only occurred at the agglomerate region of the catalyst layer. Based on the thin film-agglomerate model, the porous electrolyte (Nafion ionomer in this project) fills the pore of the catalyst layer, and in contact with the active area where heterogeneous reaction occurs. Water has higher affinity to Nafion compared to oxygen and as the result; it is difficult for oxygen to diffuse and reach the surface area once water filled the electrolyte.

Figure 5-26 High frequency response of cell with both electrodes humidified

Figure 5-24 showed that all humidification schemes exhibited similar inductance response followed by one semi circle (R-CPE) with porous system characteristics, and small inductance arc at low frequency. The exception was given by the response of anode-cathode humidification scheme for its second arc at lower frequency. The mechanisms behind the existence of first inductive, first, and second capacitive arc have been explained in Section 5.1.2.1 and above.

Compared to other set of results, it appears that the inductance arc with high time constant was articulated better when the measurement was not preceded by a preparation step. The size of this arc was reduced as measurement proceeded. Based on literature review given in Chapter 2, this second impedance arc was probably related to adsorption of gas onto the surface of catalyst pore, i.e., the first elemental step of heterogeneous reaction. The response of the last scheme showed that this second inductive arc preceded the occurrence of the second capacitive arc. The replacement was probably because the impedance for gas adsorption step, which affects the current generation initially, had become less significant. This resulted in improvement of the overall rate of mechanism occurred at the electro-active area with reaction time, as indicated by smaller magnitude of Charge Transfer Resistance. Diffusion limitation, which is responsible for the appearance of the second capacitance arc, became dominant from this point onwards. Further investigation is needed to confirm this result.

Above explanation resurfaces the previous difficulties on assigning mechanism to a particular response. So far researchers have not yet reached an agreement on which mechanism causing the occurrence of second capacitive arc at low frequency domain.

Even though in general it is agreeable that the existence of this arc was due to diffusion limitation, it is still not very clear whether this limitation occurs at anode, cathode, catalyst layer, or gas diffusion layer. The Thin Film-Agglomerate Model has been a useful tool to identify diffusion related mechanisms but more investigations are required especially when dealing with anode process.

In author's opinion, it is possible for both flooding and drying mechanism to show similar response in impedance loci due to the similar root of the problem, that is water diffusion through Nafion media, hence the magnitude of time constant. Therefore, it is necessary to carefully check the general known pattern with additional information from the observed system. Again, this case showed the need of prior knowledge and supporting database to decide on the mechanism.

In addition to the second capacitive arc, the inductive arc at low frequency has also appeared in many works related to fuel cell but unfortunately there is only handful of discussion related to this topic. This lack of reference is possibly due to difficulty in establishing the exact cause of this response. It must be noted that the lack of mathematical model will hinder the mechanism investigation which its identification will be very useful to analyze condition of fuel cell. However, the establishment of both mathematical model and experimental result database is encouraged to enhance performance analysis and control of PEM Fuel Cell.

5.3.2. The effect of Back Pressure on the Cell Performance

In this set of experiments, the effect of back pressure on anode and cathode was observed. Similar to the previous section, the current response measured at operating potential of 0.6 Volt alternating with impedance assessment for 1 hour duration. The applied potential perturbation was 10 miliVolt (RMS) with frequency range of 10 kHz – 0.1 Hz. The valves controlling the electrode exits were regulated to provide back pressure of 5 and 10 psi in the electrode compartments. In all cases, hydrogen flow at the anode side was set at 84 sccm while oxygen at 42 sccm at the cathode side. The experiments conducted under dry condition (bypass path for inlet reactants) while the cell was at room temperature. The current measurement result is shown in the Figure 5-27 below. Indices A and C are assigned to anode and cathode back pressure, respectively.

The cell without any back pressure control would reach steady state slower than the back-pressurized cell. At the beginning, it started at low current density of 67 mA/cm² and increased to reach 118 mA/cm² at the end of one hour. In general, the cells with back pressure control had higher performance compared to the base condition except the cathode only back pressure scheme. The figure also showed that when back pressure exerted on both electrodes, the cell performed better compared to when the back pressure was exerted on only one electrode. Back pressure of 10 psi delivered higher current density compared to that of 5 psi. One side wise, application of back pressure at anode gave better performance compared to application of back pressure at cathode.

Figure 5-27 Current (in current density) generated by cell at different pressure scheme

Back pressure system provides obstruction to the movement of leaving gases by means of regulating valve, thus increasing the total pressure of the electrode. In these schemes, the outlet openings were choked causing some of the gases to accumulate near the outlet orifice at the beginning to obtain the target back pressure. This would retain the coming reactants for longer time in the electrode compartment. As the result, the reactants settled for longer time at the electrode compartment and thus increase the possibility of their adsorption onto the active surface of the catalyst. More active sites would be occupied with reactants within the same initiation time, allowing faster electron generation as current was drawn from the cell. In the absence of the back pressure, the occupation of the surface active site by reactants would be slower. In addition, the back pressurized schemes were able to maintain this steady output until the end of one hour period. This is probably due to the regulatory effect caused by the back pressure. The build up of reactants in the gas diffusion layer buffered the concentration difference required for diffusion to maintain electrochemical reaction.

However, hydrogen and oxygen were not the only retained molecules in the electrode compartments since water was fed to both sides. The performance of the cathode only back pressure scheme was low compared to the base condition at the end of observation period. Back pressure in cathode caused more water vapor to condense due to larger amount of water brought from humidification chamber (assuming similar humidification level at both sides) and the water generated due to electrochemical reaction. This increased the diffusion limitation for oxygen. Hence, it lowered the cell performance. At anode, back pressure helped to condense the water vapor into liquid and replenish the water molecules brought to cathode by electro-osmotic drag.

The impedance spectra obtained from this experiment is given in Figure 5-28. The sampling times are at 2th, 14th, 26th, 38th, 50th, and 58th minutes. As time ticks, the size of the arcs decreased showing the reduction in the Charge Transfer Resistances. At the same time, the arcs shifted toward the origin indicating decrease in High Frequency Resistance. This figure once again shows that the change of cell performance recorded by current measurement method was reflected in EIS spectra. The size of impedance loci for cell without back pressure decreased slowly with time. On the other hand, other spectra reached steady state before 14th minutes showing the regulating effect of the back pressure.

Equivalent circuit parameter was used to extract the HFR and R_{ct} values of those spectra. It can be seen that the distribution of time constants due to porous surface characteristics was not significant in those responses. Therefore, simple circuit model presented in Figure 5-29 could be used with relatively high accuracy. The fitting outcome listed in Table 5-7 indicated that in general, pressurized condition exhibited lower HFR and R_{ct} than no–

pressurized condition, which resulted in higher performance compared to the base condition. Note that the higher the current density, the lower the HFR and R_{ct} will be.

Figure 5-28 Impedance spectra at different back pressure schemes

Figure 5-29 One arc equivalent circuit for the fitting of the cells response at different back pressure schemes

Table 5-8 Equivalent circuit parameter and current density for different back pressure scheme

Parameters	Base	A-C, 5 psi	A-C, 10 psi	C, 5 psi	A, 5 psi
HFR (Ω/cm^2)	0.151	0.123	0.112	0.181	0.138
R_{ct} (Ω/cm^2)	0.102	0.064	0.052	0.125	0.081
Current (mA/cm^2)	118.4	167.5	192.8	100.3	142.2

One interesting thing to note is that despite the flooding that is expected to happen due to the high condensation as the back pressure was applied to the cathode, the HFR and R_{ct} obtained were the highest compared to other data sets signifying increase in cell ohmic losses. To investigate this condition further, another set of experiment was carried out by applying 10 psi back pressure to either cathode or anode. The impedance and current obtained from this set of experiment is illustrated in Figure 5-30 below. The responses for base case condition were shown for reference.

Equivalent circuit fitting result as well as the current density recorded at the end of measurement is summarized in Table 5-9. This experiment result showed that mounting 10 psi back pressure on cathode resulted in higher HFR and R_{ct} compared to those obtained from the base case, confirming the previous outcome using 5 psi back pressure.

Apparently, the application of back pressure scheme to cathode caused more condensed water than required for proton transport. Water vapour from oxygen inlet entering the three-phase boundary and that generated from electrochemical reaction were condensed and accumulated around the reaction sites. There is possibility that this accumulation was absorbed by the surrounding Nafion since it can hold water up to 4 times of its mass, causing the ionomer at the cathode catalyst layer to swell. Hence, it lengthened the path for proton to reach membrane.

(a) 10 psi pressure applied to cathode only

(b) 10 psi pressure applied to anode only

(c) no back pressure applied

(d) Current density from base condition as well as 10 psi back pressure applied to cathode and anode

Figure 5-30 Responses of cell at one electrode only back pressure schemes

In addition, this expansion of Nafion electrolyte at the boundary condition would also present a hindrance for electrons from reaching the carbon powder particles and current collector. It is worth to note that at the surface of Gas Diffusion Layer, the catalyst was supported by the carbon powder as electronic conductor and the Nafion electrolyte fill in the pore as well as covering this agglomerate. Indeed, the optimum volume ratio between the ionomer and the carbon powder as the protonic and electronic conductor is of great significance to determine the performance of the cell. These hindrances in the proton and electron movement explained the increase of HFR, signifying the losses due to the transport of charged material, as back pressure was applied to cathode.

Table 5-9 Parameters obtained from experiments to confirm the effect of back pressure to cathode

Parameter	Base	Cathode		Anode	
		5 psi	10 psi	5 psi	10 psi
HFR (Ω/cm^2)	0.151	0.181	0.189	0.138	0.153
R_{ct} (Ω/cm^2)	0.102	0.125	0.134	0.081	0.082
Current (mA/cm^2)	118.4	100.3	98.6	142.21	139.0

This mechanism occurred as well in anode, supported by the fact that the increase in the back pressure from 5 psi to 10 psi to anode resulting in notable increase of HFR value. As mentioned previously, application of lower back pressure to the anode increased the utilization of the catalyst layer as well as increasing the proton transport due to more liquid water was available. However, further increase in back pressure caused even more water condensation at the anode TPB. At the same time, the removal of water due to the proton electro-osmotic drag remained more or less the same since there is no significant change in cell temperature and the cell potential. Therefore, there was “excess” of water at the anode catalyst region. There is possibility that, similar to the mechanism occurred at the cathode, the removal of water accumulated at the anode TPB through unreacted fuel stream was

impeded by the back pressure applied at the outlet of the cell. As the result, more water was absorbed by the Nafion phase at TPB causing increase in its size beyond that required to maintain optimum proportion of conducting phases of fuel, electron, and proton. Hence it caused reduction in the cell HFR. It appeared that there was certain optimum back pressure level to reach the highest cell performance based on the application of this scheme to anode.

When back pressure was applied to both sides of electrodes, the back pressure exerted on one electrode side is balanced by the other side, limiting the volume expansion of Nafion phase at TPB, thus maintaining the optimum volume ratio of the Nafion-carbon particle-catalyst. This two-side back pressure also facilitated the accumulated water at the three phase boundary to migrate to membrane side, which has far larger volume than the ionomer at the TPB to retain the liquid water resulting in higher proton conductivity. As the result, lower HFR can be obtained when back pressure was applied to both electrodes.

Figure 5-31 depicted the close relationship among HFR, R_{ct} , and current density for all back pressure schemes. Both HFR and R_{ct} were inversely proportional to current density as explained by Ohm's law. Furthermore, the increase in HFR due to application of one particular back pressure scheme was followed by the increase in R_{ct} . This correlation implied the close interrelationship between the proton conduction at the membrane electrolyte and electrolyte covering the agglomerate region under steady state.

Figure 5-31 HFR, Rct, and current density value obtained from different schemes of applied back pressure

Conclusion and Suggestion

6.1. Conclusion

Analysis of PEM Fuel Cell performance using two in-situ non destructive electrochemical assessment methods namely Current Measurement Method and Electrochemical Impedance Spectroscopy was capable of revealing the probable mechanisms occurred within the cell and the key factors affecting the cell performance. In addition, the introduction of two novel methods was proven to yield higher analysis capability. The use of segmented fuel cell enabled detailed observation of effect of flow channel design and operating condition on cell local activity. Thin Film-Agglomerate model was capable of identifying underlying mechanisms differentiating the oxygen and air cell performance which could not be resolved by current measurement and EIS.

Locally resolved assessment using segmented fuel cell revealed that topological design of flow channel facilitating distribution of reactants and operating parameters over the surface-active area influence the magnitude and distribution pattern of current density significantly. The cell performance of Parallel, 1-S, and 3-S flow channel topologies were observed. Parallel flow field showed the poorest averaged current and distribution while 3-S topology was capable of maintaining the highest average current and its homogeneity. Compared to 1-P topology, 3-S design has higher pressure to force reactants to reach catalyst layer due to its meandering flow field characteristics. It also has shorter flow path from the inlet to the outlet than 1-S flow field (approximately one third) resulting in lower

water drag effect, thus helps to prevent membrane from dehydration, and lower pressure drop for more effective reactants distribution.

Impedance spectra study from the segmented fuel cell in 8-segments mode in potential range of OCV – 0.5 Volt showed that at certain cell potential, all segments underwent similar mechanisms but of different magnitude. This was probably because flooding did not occur for the potential range observed and as the result, the segments rank for current density magnitude remained the same for all cell potential. The group of segments located at the peripheral performed better compared to that located at the center. One reason for this was the first group of segments was positioned at or close to reactants inlets. This group was also benefited by its short distance from bracing bolts located at the four edges of fixtures hence reducing the contact resistance. The value of HFR was constant for all cell potential while R_{ct} decreased fast as the potential decreased. It appeared that the water generated in reaction affected the proton conductivity of the TPB and was not able to affect that of membrane due to its small volume produced. In addition, the activation/preparation step done prior to the main experiment was considered necessary to humidify the membrane.

There are four common mechanisms observed from the impedance response of the segments as well as cells used in this project; inductive response of measurement device, Faradaic reaction, diffusion, and reactants adsorption. Mostly, the second capacitive arc indicating limitation for Faradaic reaction exhibited porous electrode response as linear region at higher frequency part of the arc appeared. It is emphasized in the result that pattern recognition and prior knowledge on the cell behavior are required to assign certain mechanism in corresponding to the spectra generated by the cell.

Current measurement and impedance registration for oxygen and air cells showed that both cells demonstrated distinguishable responses but the diffusion problem arising from the introduction of inert gas nitrogen in air was not observable. Data manipulation and interpretation based on Thin-Film Agglomerate model were able to isolate the mechanisms occurred within both cells. The plot $\log (R_t^{-1})$ vs. cathode potential of oxygen cell exhibited three curves with different slopes indicating high, middle, and low cathode potential range with their dominant mechanisms; Faradaic reaction, lack of oxygen supply at agglomerate region, and diffusion limitation over the thin film region. The first slope and the second slope of air cell were comparable in magnitude to the oxygen one. The third slope of the air cell, on the other hand, was significantly higher than the oxygen cell counterpart, indicating that in that cell potential range, thin film diffusion played an important role in the air cell. In addition to these three slopes, air cell exhibited the fourth slope whose slope, unlike others, was positive. This slope could be associated with diffusion limitation in the gas diffusion layer, indicating further performance loss due to oxygen transport.

Various humidification schemes were applied to the cell using 1-S flow field and 7.5 cm^2 operating at 84 sccm H_2 and 42 sccm O_2 . During two hours period of observation, all cell under different schemes progressed towards smaller HFR and R_{ct} indicating increase in cell humidity level. The performance of the cell increased from no humidification scheme, cathode-only humidification, anode-only humidification, to both-electrodes humidification scheme. The reason behind this is that inlet humidification provides additional water content improving proton conductivity. Another factor for this is the elevated reactants temperature due to contact with higher temperature water in humidifier chamber. This factor is beneficial for the reactants to overcome the energy activation barrier. As far as diffusion is concerned, the rate of proton transport within Nafion is exponential with the

increase of temperature. Anode humidification has higher impact on cell performance than cathode humidification due to difference in water supply mechanisms occur at each electrode. Both-electrodes humidification scheme exhibited additional LF arc attributed to oxygen diffusion limitation due to water accumulation at the cathode GDL by considering the high humidification condition and lowering HFR value as the experiment proceeded.

Application of back pressure to cell (1-S flow field and 7.5 cm^2 operated at 84 sccm H_2 and 42 sccm O_2) without humidification resulted in higher cell performance output. Higher back pressure (10 psi) gave higher current density compared to the lower back pressure (5 psi). This is because back pressure imposes longer reactants retention time and higher utilization of surface active area can be obtained. Application of back pressure at anode facilitates water condensation advantageous for proton transport. However, at cathode this back pressure imposes hindrance on water leaving the catalyst layer hence causing expansion/swelling of the electrolyte, thus repelling the electron conducting-carbon powder material. This causes HFR to increase as evidenced from the impedance spectra. When back pressure is mounted on both sides, the back pressure at anode provides the pressure to encounter this swelling effect thus higher performance can be obtained.

6.2. Suggestion for Future Improvement

Current Measurement and EIS for performance analysis purpose had been proven capable of indicating and explaining factors affecting the performance of PEM Fuel Cell. Application of those techniques to segmented fuel cell enables locally resolved cell performance observation to advance fundamental knowledge of fuel cell phenomena. Thin Film-Agglomerate Model has also shown its potential in isolating diffusion-related mechanisms which are irresolvable by general electrochemical methods. However, the complicated and interrelated nature of processes occurring within the PEMFC demands

further advancing identification and analysis technique. Therefore, some suggestions for improvement based on current results are proposed.

1. Improvement on experiment design using segmented fuel cell in order to extract more information from the cell under testing. This includes the use of multipotentiostat to observe degradation development as a function of time as well as to reduce current spreading for higher accuracy in measurement, improvement in fixture design and material for better contact pressure, and incorporation of temperature monitoring method (e.g. thermography) to facilitate energy analysis.
2. Development of mechanism database for PEM Fuel Cell. Comprehensive records and observation of various PEMFCs responses leading to mechanisms database will significantly advance the performance analysis and pattern recognition process for this highly nonlinear system. It is expected that this database will also help to establish understanding on phenomena occurring within the cell, e.g. the nature of the second capacitive (LF) impedance arc.
3. The use of Thin Film-Agglomerate Model to isolate anode mechanisms. So far the use of this model focuses on cathode performance observation since it is known that cathode processes are the main limiting factors for the cell performance. Since it is also known that significant increase in anode overpotential can occur under high current density or in the presence of fuel impurities, the use of TFA model for further observation on anode losses will be of high significance
4. Incorporation of other methods to achieve higher analysis accuracy. The use of ex-situ as well as *post mortem* (destructive) testing, e.g. cyclic voltammetry, chemical, and morphology testing, can provide substantial supporting information to understand the factors contributing to cell characteristics and the strategies to improve cell performance.

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Flow Field Topology Designs

Figures A-1 to A-3 show the flow field designs for the sets of experiments explained in section 5.1 on segmented fuel cell. The numbering begins from the segment close to oxygen inlet at the top row to the segment near oxygen outlet at the bottom. In the later part of measurement, this numbering was changed into 8-segment mode (shown in figure 5-6). These figures are captured from cathode side. Figure A-4 shows the inner and outer surface of the segmented fixture (3-S). The last figure (A-5) shows the segmented fuel cell setup with manual switch in 8-segment mode.

Figure A-1 Parallel Flow Field

Figure A-2 1-line Serpentine Flow Field (1-S)

Figure A-3 3-line Serpentine Flow Field (3-S)

Figure A-4 Segmented Fuel Cell Fixture (3-S); inner surface (left) and outer surface (right)

Figure A-5 Segmented fuel cell setup with manual switch in 8-segment mode

Impedance Spectra of Elements Describing Mechanisms in PEMFC

The impedance responses of equivalent circuit elements generally used to represent mechanisms in the PEM Fuel Cell is illustrated below in Nyquist diagram. Impedance of all elements but resistive element is affected by measurement frequency.

1. Resistance (R), $Z_R = R$

Figure B-1 Impedance Responses of Resistive Component, simulated in frequency range $10^{-1} - 10^4$ Hz

2. Inductance (L), $\mathbf{Z_L = i\omega L}$

Figure B-2 Impedance Response of Inductive Element, $L = 10^{-3}$ H, simulated in frequency range $10^{-1} - 10^4$ Hz

3. Capacitance (C), $\mathbf{Z_C = (i\omega C)^{-1}}$

Figure B-3 Impedance Response of Capacitive Element, $C = 10^{-1}$ F, simulated in frequency range $10^{-1} - 10^4$ Hz

4. Constant Phase Element (CPE), $Z_{CPE} = T^{-1}(i\omega)^{-n}$

Note that if $T^{-1} = \sigma$ and $n = 0.5$, $Z_{CPE} = Z_W$.

$Z_W = \sigma(i\omega)^{-0.5}$ represents the Warburg diffusion element.

Figure B-4 Impedance Response of Constant Phase Element (CPE), $T = 0.1$ (unit depends on n), simulated in frequency range $10^{-1} - 10^4$ Hz

5. Nernst/Finite Diffusion, $Z = (i\omega)^{-0.5} \tanh(i\omega R^2/\sigma)^{0.5}$

Figure B-5 Impedance Responses of Nernst/Finite Diffusion arc, $R = 100 \Omega$, $\sigma = 0.01 \Omega$, simulated in frequency range $10^{-3} - 10^4$ Hz

Impedance Spectra of Capacitive Arc at Different R_{ct} and C_{dl} Values

Responses of capacitive arcs of different parallel resistance (R_p) and capacitance (C) values are illustrated in figure C-1 to C-3. The general term R_s (series resistance) is used instead of HFR to generalize the intercept of the arc with Z_{Re} axis.

1. Variation of R_{ct} (R_p) values

In PEM Fuel Cell, parallel resistance (R_p) of high frequency arc is well known as R_{ct} . The value of this resistance is equal to the diameter of the capacitive arc and determines the size of the arc.

Figure C-1 Impedance responses of capacitive arc at different R_p values,
 $R_s = 0.1 \Omega$, $C_{dl} = 0.1 F$, simulated in frequency range $10^{-1} - 10^4$ Hz

2. Variation of Double Layer Capacitance (C_{dl}) values

Figure C-2 illustrates that C_{dl} values do not affect the arcs diameter. For the same frequency range, arc with higher C_{dl} value exhibits less arc-like appearance.

Figure C-2 Impedance responses of capacitive arc at different double layer capacitance values, $R_s = 0.1\Omega$, $R_p = 0.5\Omega$, simulated in frequency range $10^{-1} - 10^4$ Hz

3. Comparison between Pure Capacitive Arc and CPE arcs

For solid-solid system like PEMFC, Constant Phase Element (CPE) is often used instead of pure capacitance to take into account the surface roughness and inhomogeneities of the interfaces.

Figure C-3 Impedance responses of R-C and R-CPE arc, $C = T = 0.3$ (unit depends on n), $R_s = 0.1\Omega$, $R_p = 0.2\Omega$, simulated in frequency range $10^{-1} - 10^4$ Hz

Equivalent Circuit Fitting for 8-Segment Mode Segmented Fuel Cell

Tables below itemize the parameters obtained from fitting of the 8 segments impedance data at potential range OCP – 0.5 Volt. This result was explained in section 5.1.2.2 and the equivalent circuit used was shown in figure 5-10.

1. At Open Circuit Potential (OCP)

Segment	HFR ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)	T_1	n_1	T_2	n_2
S1	0.041	22.676	1.139	0.599	0.765	0.981
S2	0.043	32.326	0.932	0.617	0.748	0.962
S3	0.105	28.086	1.276	0.565	0.745	0.969
S4	0.141	34.714	1.013	0.559	0.738	0.960
S5	0.128	32.304	1.510	0.528	0.737	0.963
S6	0.148	34.611	1.090	0.543	0.733	0.961
S7	0.073	28.532	1.597	0.478	0.738	0.974
S8	0.056	25.713	1.331	0.556	0.736	0.981
StDev	0.044	4.341	0.236	0.043	0.010	0.009
Average	0.092	29.870	1.236	0.556	0.743	0.969
StD/Avg	0.481	0.145	0.191	0.077	0.014	0.009

2. At 0.9 Volt

Segment	HFR ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)	T_1	n_1	T_2	n_2
S1	0.041	9.216	1.129	0.606	0.785	0.984
S2	0.043	9.389	1.048	0.595	0.778	0.972
S3	0.104	10.158	1.344	0.560	0.774	0.973
S4	0.140	11.541	0.946	0.581	0.765	0.962
S5	0.125	11.298	1.216	0.557	0.765	0.966
S6	0.148	12.124	1.168	0.537	0.761	0.965
S7	0.070	11.095	1.874	0.448	0.771	0.983
S8	0.056	11.358	1.316	0.565	0.765	0.981
StDev	0.044	1.059	0.282	0.049	0.008	0.009
Average	0.091	10.772	1.255	0.556	0.770	0.973
StD/Avg	0.483	0.098	0.225	0.088	0.011	0.009

3. At 0.8 Volt

Segment	HFR ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)	T_1	n_1	T_2	n_2
S1	0.041	0.460	1.325	0.598	1.249	1.000
S2	0.043	0.456	1.202	0.584	1.163	1.000
S3	0.103	0.501	1.599	0.553	1.111	1.000
S4	0.137	0.532	1.297	0.537	1.048	0.991
S5	0.121	0.512	1.727	0.513	1.050	0.997
S6	0.145	0.541	1.542	0.499	1.058	0.995
S7	0.069	0.490	2.048	0.446	1.097	0.987
S8	0.056	0.446	1.377	0.574	1.193	1.000
StDev	0.043	0.036	0.277	0.051	0.074	0.005
Average	0.089	0.492	1.515	0.538	1.121	0.996
StD/Avg	0.477	0.072	0.183	0.094	0.066	0.005

4. At 0.7 Volt

Segment	HFR ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)	T_1	n_1	T_2	n_2
S1	0.041	0.116	1.071	0.662	0.792	0.926
S2	0.043	0.117	0.711	0.688	0.848	0.934
S3	0.100	0.127	0.926	0.656	0.954	0.948
S4	0.135	0.137	0.620	0.674	1.084	0.916
S5	0.124	0.135	0.930	0.623	1.057	0.951
S6	0.147	0.135	0.857	0.608	1.260	0.971
S7	0.069	0.123	0.951	0.574	0.991	0.890
S8	0.054	0.099	0.846	0.662	1.209	0.932
StDev	0.043	0.013	0.142	0.038	0.163	0.024
Average	0.089	0.124	0.864	0.643	1.024	0.933
StD/Avg	0.043	0.013	0.142	0.038	0.163	0.024

5. At 0.6 Volt

Segment	HFR ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)	T_1	n_1	T_2	n_2
S1	0.044	0.071	0.670	0.767	0.867	0.889
S2	0.051	0.070	0.580	0.746	0.904	0.897
S3	0.106	0.085	0.903	0.682	1.082	0.940
S4	0.137	0.085	0.777	0.670	1.318	0.930
S5	0.119	0.091	0.941	0.650	1.209	0.908
S6	0.133	0.087	0.797	0.671	1.311	0.889
S7	0.065	0.081	0.891	0.616	1.099	0.907
S8	0.051	0.058	0.785	0.716	1.414	0.876
StDev	0.040	0.011	0.122	0.050	0.198	0.022
Average	0.088	0.079	0.793	0.690	1.150	0.905
StD/Avg	0.449	0.142	0.154	0.073	0.172	0.024

6. At 0.5 Volt

Segment	HFR ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)	T_1	n_1	T_2	n_2
S1	0.044	0.041	0.484	0.853	0.991	0.847
S2	0.049	0.042	0.420	0.827	0.993	0.859
S3	0.113	0.065	0.740	0.698	1.089	0.920
S4	0.156	0.075	0.386	0.817	1.054	0.727
S5	0.125	0.068	0.915	0.667	1.208	0.880
S6	0.134	0.087	0.002	1.000	1.014	0.679
S7	0.064	0.058	0.458	0.747	1.123	0.768
S8	0.051	0.035	0.475	0.880	1.299	0.768
StDev	0.045	0.018	0.267	0.107	0.110	0.083
Average	0.092	0.059	0.485	0.811	1.096	0.806
StD/Avg	0.485	0.313	0.550	0.132	0.100	0.103

Equivalent Circuit Fitting for Thin Film-Agglomerate Model

Tables below itemize the parameters obtained from fitting of impedance data (at potential range OCV – 0.24 Volt) of cells running on oxygen and air for the Thin Film – Agglomerate model. This approach was explained in section 5.2 and the equivalent circuit used was shown in figure 5-10.

1. The Equivalent Circuit Fitting Result for Oxygen Cell

Parameter	OCV	0.88V	0.84V	0.8V	0.76V	0.72V
HFR ($\Omega \cdot \text{cm}^2$)	0.242	0.192	0.191	0.191	0.191	0.191
R_t ($\Omega \cdot \text{cm}^2$)	0.950	0.753	0.454	0.302	0.215	0.167
T_1	0.575	0.580	0.427	0.325	0.250	0.220
n_1	0.494	0.541	0.573	0.603	0.631	0.644
T_2	0.136	0.141	0.119	0.102	0.085	0.074
n_2	0.905	0.904	0.927	0.945	0.959	0.964

Parameter	0.68V	0.64V	0.6V	0.56V	0.52V	0.48V
HFR ($\Omega \cdot \text{cm}^2$)	0.191	0.191	0.193	0.194	0.196	0.193
R_t ($\Omega \cdot \text{cm}^2$)	0.138	0.121	0.109	0.102	0.094	0.089
T_1	0.203	0.209	0.235	0.268	0.241	0.286
n_1	0.652	0.649	0.638	0.625	0.651	0.638
T_2	0.065	0.059	0.057	0.056	0.059	0.065
n_2	0.970	0.966	0.962	0.955	0.975	0.945

Parameter	0.44V	0.4V	0.36V	0.32V	0.28V	0.24V
HFR ($\Omega \cdot \text{cm}^2$)	0.192	0.192	0.194	0.194	0.195	0.196
R_t ($\Omega \cdot \text{cm}^2$)	0.085	0.085	0.082	0.081	0.079	0.077
T_1	0.274	0.274	0.292	0.273	0.292	0.309
n_1	0.636	0.636	0.633	0.638	0.631	0.630
T_2	0.065	0.065	0.071	0.078	0.086	0.092
n_2	0.971	0.971	0.979	1.000	1.000	1.000

2. The Equivalent Circuit Fitting Result for Air Cell

Parameter	OCV	0.88V	0.84V	0.8V	0.76V	0.72V
HFR ($\Omega \cdot \text{cm}^2$)	0.162	0.161	0.161	0.162	0.162	0.163
R_t ($\Omega \cdot \text{cm}^2$)	1.556	1.205	0.746	0.508	0.390	0.328
T_1	2.110	2.320	1.840	1.280	1.140	0.975
n_1	0.381	0.361	0.382	0.433	0.443	0.467
T_2	0.252	0.238	0.228	0.218	0.208	0.198
n_2	0.825	0.819	0.795	0.793	0.793	0.802

Parameter	0.68V	0.64V	0.6V	0.56V	0.52V	0.48V
HFR ($\Omega \cdot \text{cm}^2$)	0.159	0.162	0.162	0.161	0.164	0.166
R_t ($\Omega \cdot \text{cm}^2$)	0.313	0.290	0.275	0.277	0.268	0.266
T_1	1.490	1.120	1.040	1.550	0.984	1.060
n_1	0.394	0.448	0.457	0.393	0.471	0.473
T_2	0.197	0.190	0.192	0.208	0.201	0.197
n_2	0.788	0.805	0.804	0.780	0.803	0.826

Parameter	0.44V	0.4V	0.36V	0.32V	0.28V	0.24V
HFR ($\Omega \cdot \text{cm}^2$)	0.166	0.171	0.167	0.167	0.170	0.175
R_t ($\Omega \cdot \text{cm}^2$)	0.269	0.266	0.277	0.286	0.288	0.302
T_1	0.910	0.713	2.090	2.790	2.510	1.100
n_1	0.496	0.551	0.386	0.346	0.367	0.503
T_2	0.194	0.198	0.200	0.206	0.200	0.206
n_2	0.843	0.860	0.813	0.800	0.813	0.910