The Pennsylvania State University
The Graduate School
College of Earth and Mineral Sciences

DEVELOPMENT AND CHARACTERIZATION OF DIRECT ETHANOL FUEL CELLS USING ALKALINE ANION-EXCHANGE MEMBRANES

A Dissertation in
Materials Science and Engineering
By
Peck Cheng Lim

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ABSTRACT

Alkaline membrane fuel cell (AMFC) is a relatively new fuel cell technology that is generating considerable interests. It offers the electrocatalytic advantages of conventional alkaline fuel cells, and the manufacturing and cost advantages of solid polymer electrolyte fuel cells. This project was carried out to develop and characterize high performance membrane electrode assemblies (MEAs) for all-solid-state AMFCs. The primary fuel of interests is ethanol, but hydrogen was used in the development stages to facilitate the diagnostic and evaluation of the fuel cell performance.

In the preliminary investigation, AMFC was assembled using off-the-shelf electrodes and anion-exchange membrane (AEM). It was found that the performance of AMFC operating on ethanol fuel was limited by a large high-frequency resistance (HFR) value. The advantage of using non-toxic ethanol fuel was also compromised by the need to add hydrazine and potassium hydroxide to the fuel blend.

Subsequently, a high performance MEA was developed for an all-solid-state AMFC, in which liquid electrolyte or other additives were not required during the operation of the fuel cell. Ionomer was incorporated in the formulation of catalyst ink, and the catalyst ink was directly coated on the anion-exchange membrane (AEM). An ionomer content of 20 wt.% was found to be the optimum amount required in the catalyst layers. It was demonstrated that the AMFC generated a maximum power density of 365 mW/cm² and 213 mW/cm² with the use of hydrogen/oxygen and hydrogen/pure air, respectively. The performance of the AMFC was also found to be influenced by exposure to carbon dioxide in the air. Hence, the CCMs were pre-treated in potassium
hydroxide solution and pure oxygen was used to condition the fuel cell to maximize the power output from the AMFCs. Although satisfactory performance was demonstrated in the AMFC, its stability during cell operation remains a major issue. The poor stability was attributed to degradation of ionomer in the catalyst layers, especially at the catalyst/ionomer interfaces.

Ethanol was also used as a fuel in the AMFC with newly developed MEAs. Wet-proof gas diffusion layers (GDLs) was found to enhance mass transport in liquid-fed AMFC. With the use of 1M ethanol, the AMFC exhibited a maximum power density of 6.482 mW/cm² and 3.380 mW/cm² with pure oxygen and ambient air as oxidant, respectively. These maximum power density values are the highest reported to-date. However, significant work is still necessary in advancing the AMFC technology for direct alcohol fuel cell applications.
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\( n_{\text{out}} \)  \( n_{\text{produced}} \)  \( n_{\text{transport}} \)  

Number of mole of water in outlet [mol]  
Number of mole of water produced at anode [mol]  
Number of mole of water transported [mol]  

\( p_{\text{air}} \)  \( p_{\text{H}_2} \)  \( p_{\text{O}_2} \)  \( p_{\text{oxidant}} \)  \( p_{\text{pure air}} \)  

Air pressure [atm]  
Hydrogen pressure [atm]  
Oxygen pressure [atm]  
Oxidant pressure [atm]  
Pure air pressure [atm]  

\( R \)  \( R_{\text{H}_2} \)  \( R_{\text{N}_2} \)  \( R_{\text{O}_2} \)  \( R_{\text{oxidant}} \)  \( R_{\text{pure air}} \)  

Resistance [Ω]  
Relative humidity of hydrogen [%]  
Relative humidity of nitrogen [%]  
Relative humidity of oxygen [%]  
Relative humidity [%]  
Relative humidity of pure air [%]  

\( T_{\text{cell}} \)  \( V_{\text{40\%Pt/C}} \)  \( V_{\text{Catalyst Layer}} \)  \( V_{\text{ionomer}} \)  \( V_{\text{pore}} \)  

Cell temperature [°C]  
Volume of carbon support [cm³]  
Volume of catalyst layer [cm³]  
Volume of ionomer [cm³]  
Total pore volume [cm³/g]  

\( x \)  \( x_{\text{cp}} \)  

Mass fraction  
Mass fraction of porous carbon
$x_p$ Mass fraction of platinum

$\%porosity$ Porosity level

$\alpha$ Net water transport coefficient

$\rho$ Density [g/cm$^3$]

$\rho_{40\%Pt/C}$ Density of 40 wt.% platinum on porous carbon support [g/cm$^3$]

$\rho_{80\%Pt/C}$ Density of 80 wt.% platinum on porous carbon support [g/cm$^3$]

$\rho_{80\%PtRu/C}$ Density of 80 wt.% platinum-ruthenium on porous carbon support [g/cm$^3$]

$\rho_{ionomer}$ Density of ionomer [g/cm$^3$]

$\rho_c$ Density of carbon [g/cm$^3$]

$\rho_{Cp}$ Density of porous carbon [g/cm$^3$]

$\rho_{Pt}$ Density of platinum [g/cm$^3$]

$\nu$ CV scan rate [mV/s]

**Acronyms**

AEM Anion-exchange membrane

AFC Alkaline fuel cell

AMFC Alkaline membrane fuel cell

CCM Catalyst-coated membrane

CCS Catalyst-coated substrate

CE Counter electrode

CL Catalyst layer

CV Cyclic voltammetry or cyclic voltammogram
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DEFC</td>
<td>Direct ethanol fuel cell</td>
</tr>
<tr>
<td>DL</td>
<td>Double layer</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
</tr>
<tr>
<td>ECA</td>
<td>Electrochemically active area</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>HFR</td>
<td>High-frequency resistance</td>
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<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MEM</td>
<td>Membrane</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous layer</td>
</tr>
<tr>
<td>OCV</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton-exchange membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton-exchange membrane fuel cell</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>STP</td>
<td>Standard temperature and pressure</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

Like all the essential components required in a fuel cell to make it work, the completion of this dissertation is possible because of the guidance, support and encouragement of several key people I worked with throughout the duration of this project.

First and foremost, I would like to express my gratitude to my advisor, Distinguished Professor Chao-Yang Wang, for his guidance and insightful discussions given over the length of this work. Thanks are also due to Dr Shanhai Ge from the Electrochemical Engine Center for providing many fruitful discussions and suggestions during this work. The many productive discussions with Professor Michael Hickner and Dr Jingling Yan from the Department of Materials Science and Engineering, as well as Mr Hiroyuki Yanagi, Mr Kenji Fukuta and their team from Tokuyama Corporation are greatly appreciated.

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Finally, let me extend my heartfelt appreciation to my family and friends for their support, understanding and encouragement through this amazing journey.
CHAPTER 1

INTRODUCTION

1.1 An Overview on Alternative Energy Sources

With an increasing world population and advances in civilization, the energy consumption in the 20th century was marked with an unprecedented high [1]. This trend of increasing energy consumption is likely to continue in the 21st century. Coupled with rapidly diminishing conventional energy sources, predominately based on fossil fuels, this increasing demand on energy has prompted various efforts around the world to explore alternative methods in harvesting energy. In particular, clean alternative energy sources are strongly preferred due to heightened awareness on the protection of the environment.

Electrochemical power generation is one of the alternative energy-harvesting technologies that is attracting considerable interest due to its sustainability and environmental friendliness [2]. Two of the major systems for converting chemical energy into electrical energy are batteries and fuel cells. Batteries and fuel cells are essentially similar in nature; the chemical processes occur at the electrodes and the flow of electronic and ionic species are separated by an electrolyte.

A battery is a self-contained unit in which chemical energy is stored within the unit. Hence, the operation of batteries is limited by its storage capacity. This finite energy storage capacity is a key disadvantage in the use of batteries. In some cases, the energy can be restored in a battery by recharging. However, this often translates into
downtime in which the operation of the system that the battery is powering is restricted. This restriction makes battery power less than an ideal alternative power source, especially in the fast-paced and mobile consumer market of today. On the contrary, a fuel cell derives its power from the fuel supplied, which can be replenished almost instantaneously upon exhaustion. Hence, the fuel cell presents itself as a great energy system which can be refilled and ready to go without prolonged downtime.

The storage capacity of common types of batteries is reported to reach a maximum value of 500 Wh/L [2]. This value is close to a third of the theoretical energy density available in the most advanced battery system, such as the lithium ion battery (theoretical energy density of 1690 Wh/L). In contrast, the energy density available in fuel cell systems range from 2600 Wh/L in liquid hydrogen fuel to 4600 Wh/L in methanol fuel to 6100 Wh/L in ethanol fuel. These considerably higher energy density values allow more room for technological advancement, and further strengthen the potential of fuel cells as a clean and efficient alternative energy source of the future.

1.2 Fuel Cell Technology

Fuel cells are galvanic cells, in which the free energy of a chemical reaction is directly converted into electrical energy [3]. The simplest construction of a fuel cell is a receptacle containing a pair of electrodes and an electrolyte as first demonstrated by Sir William Grove in 1839 (see Figure 1a). Since then, the fuel cell technology has evolved substantially. However, the fundamental components in a modern, advanced fuel cell remain unchanged. Figure 1b shows a typical construction of a hydrogen proton-
exchange membrane fuel cell (PEMFC). The electrode has further evolved into multi-layers consisting of:

1. end-plane with integrated flow channels to supply fuel or oxidant uniformly throughout the cell

2. diffusion layer to further enhance the distribution of fuel or oxidant to the catalytic sites

3. catalyst layer, optimized to provide maximum number of catalytic sites available for the reactions in the cell

In PEMFC, the electrodes are separated by a solid polymer electrolyte, which function just like a liquid electrolyte in facilitating the transport of protons generated in the chemical reactions.

As in the name, the fuel cell technology will be discussed in greater detail in the following sections by examining 1) the types of fuel used in the fuel cells, 2) the types of cell construction, and 3) the types of technology employed in the manufacturing of the fuel cells.

1.2.1 Fuel: Hydrogen, Methanol and Ethanol

Hydrogen (H₂) is widely touted as a clean alternative energy source for the 21st century and has been often used in fuel cells [4, 5]. The oxidation of hydrogen occurs readily on platinum catalysts and the kinetics of oxidation process is rapid. However, hydrogen is a gas under ambient conditions and its storage remains a major challenge in utilizing hydrogen in fuel cell applications [6]. As a consequence of its bulky storage
system, hydrogen is best used in automotive applications where system size is not a critical consideration. One of the methods of eliminating the storage of gaseous hydrogen is alcohol reforming on board the fuel cell system. However, the reforming process adds to the complexity of a fuel cell system and increases the system size. Hence, the scaling down of hydrogen fuel cells for portable applications remains a difficult task.

Due to the ease of handling and storing of liquid fuel, fuel cells that harness the potential of direct oxidation of liquid alcohol appear to be the leading candidate for portable applications. Direct methanol fuel cell (DMFC) relies on the direct adsorption and oxidation of methanol (CH$_3$OH) on platinum-based anode, and the reduction of oxygen on platinum cathode to convert chemical energy into electrical energy [7]. In the acidic environment present in DMFC, very few electrode materials are capable of absorbing and oxidizing methanol effectively. Hence, the oxidation of methanol is often plagued by sluggish reaction kinetics.

Ethanol (C$_2$H$_5$OH) is another liquid fuel that can be used in direct alcohol fuel cells [8]. Ethanol is less toxic than methanol and can be made readily available through existing infrastructure of the consumer market. Another important attribute of ethanol is that it can be derived from crops such as corn and sugarcane. This makes ethanol a sustainable energy resource that could offer environmental and long-term economical advantages. However, as in methanol fuel, ethanol is plagued by sluggish electrokinetics in acidic fuel cells. In addition, the carbon-carbon bond existing in ethanol often results in incomplete oxidation.
1.2.2 Cell: Solid and Liquid Electrolytes

Fuel cells are generally grouped according to their operating temperatures and they are often named based on one of the key components in the fuel cell construction – electrolyte [9]. Major types of fuel cells, their operation and characteristics are summarized in Table 1.

A solid oxide fuel cell (SOFC) uses oxide anions ($O^{2−}$) in the ceramic-based electrolyte as the charge carrier in the cell’s redox reactions. In a molten carbonate fuel cell (MCFC), the required charge transport is fulfilled by carbonate anions ($CO_3^{2−}$). Both MCFC and SOFC operate at elevated temperatures in the range of 550 to 900°C. The operation at high temperatures facilitates fast electrode kinetics and allows high efficiencies to be attained in these fuel cells. However, the high operating temperatures also put severe constraints on the material requirement and system life. In addition, the fuel cells are plagued by slow start-up. Hence, SOFC and MCFC are best suited for stationary power generation with minimum startup/shutdown cycle.

Intermediate temperature fuel cells, such as phosphoric acid fuel cell (PAFC), operate best at about 200°C. Protons ($H^+$) in the acidic electrolyte complete the charge transport in the redox processes. PAFC easily fulfills the mid range power requirement with a high fuel efficiency and is available commercially.

An alkaline counterpart to PAFC in the form of alkaline fuel cell (AFC) operates at lower temperatures ranging from 50 to 200°C. Hydroxide anions ($OH^−$) in aqueous alkaline electrolyte can be easily replaced by carbonate ($CO_3^{2−}$) and bicarbonate anions
(HCO$_3^-$), which reduce the electrolyte conductivity. Hence, carbon dioxide (CO$_2$) in the fuel and oxidant severely reduces the performance of AFC.

In recent years, significant advancement has been made in low temperature fuel cells with the advent of solid polymer electrolyte, in particular Nafion membrane. PEMFC and DMFC utilize the transport of protons in the polymer electrolyte as the charge carrier. Hence, the use aqueous electrolyte is eliminated, which greatly simplify the fuel cell design. PEMFC and DMFC are chiefly similar in fuel cell construction. The key difference is in the types of fuel used in the cell - hydrogen in PEMFC and methanol in DMFC. Both fuel cells are generally operated at 60 to 90°C and the electrode kinetics is slower at these temperatures. Hence, high catalyst loading, especially in DMFC, is necessary and inherently increases the cost of the fuel cells.

A counterpart to proton-exchange membrane (PEM) in the form of anion-exchange membrane (AEM) is recently developed specifically for fuel cell applications. Alkaline membrane fuel cells (AMFCs) using AEMs is still in its infancy stage with major limitations such as low ionic conductivity and poor membrane stability. However, AMFC possesses several key attributes such as faster electrode kinetics, and low-cost membrane and possible use of low-cost catalysts [10].

1.2.3 Technology: Fabrication of Membrane Electrode Assembly

The making of a fuel cell relies on the integration of electrode and electrolyte to create a large electrode/electrolyte interface for catalytic reactions. In solid polymer electrolyte fuel cells, the core of fuel cell technology lies in making of membrane
electrode assembly (MEA) in which the membrane and the electrodes are integrated [11]. In essence, the MEA consists of multiple layers of materials – anode gas diffusion layer (GDL), anode catalyst layer (CL), ionomeric membrane, cathode catalyst layer and cathode gas diffusion layer. The procedure of assembling the MEA can generally be classified into two techniques, namely catalyst-coated membrane (CCM) or catalyst-coated substrate (CCS). As implied by the name, catalyst is coated directly on the membranes in CCM technique while catalyst is coated directly on substrates such as GDLs in CCS technique.

In both techniques, a crucial procedure is the formulation of catalyst ink. The catalyst ink primarily consists of catalyst supported on carbon particles and ionomer. The ink is applied to achieve large amount of catalytic sites and facilitate the transport of fuel, oxidant, and electronic and ionic species involved in the chemical reactions. Figure 2 shows an idealized interfacial structure required to provide the catalytic sites and paths for the transport of material and species. A high performance catalyst layer can be achieved with a specific ratio of catalyst, ionomer and porosity. Solvent and additives are often added to the catalyst ink to achieve a consistent and homogenous ink for spray coating or screen printing.

1.3 Motivation of the Study

Automotive and consumer electronic industries are the main drivers in fuel cell development. In particular, the development of low temperature fuel cells using PEM. Though the development of PEM-based fuel cells has evolved substantially, its
commercialization is challenged by a number of issues. One of the challenging issues is the cost of the fuel cells, with a significant portion coming from expensive platinum. In addition to platinum-based catalysts, corrosive-resistant materials are necessary in the construction of the fuel cell due to the harsh acidic environment present in the cell. The high-cost of PEM, predominantly Nafion membrane, also add to the overall cost of the fuel cell. The high cost associated with PEM-based fuel cells provides the motivation to examine other solid polymer membrane for fuel cell applications.

AEM is predominantly made up of hydrocarbon backbone and quaternary ammonium groups as ion exchanging sites. The hydrocarbon-based membrane is potentially cheaper than Nafion membrane. In addition, the alkalinity of the membrane offers the advantages of conventional AFC without problems associated with liquid electrolyte. In essence, AMFC using AEM potentially offers attractive attributes that include

(1) faster electrode kinetics in alkaline condition
(2) use of cheaper materials for catalytic and other accessorial components in the fuel cell due to less corrosive alkaline condition in AMFC
(3) use of non-platinum group metals with higher selectivity to minimize the detrimental effect of fuel crossover
(4) use of a wide selection of fuels, including ethanol which is superior than methanol in portable application and hydrogen in automotive application
1.4 Objectives of the Study

The primary objective of this study is to develop an all-solid-state AMFC for low temperature applications. This is carried out with a series of work with the following aims:

(1) to gain basic understanding of AMFC by evaluating the performance of AMFC assembled using off-the-shelf components

(2) to develop and characterize high performance MEAs for AMFC applications
Table 1  Major types of fuel cells and its characteristics.

<table>
<thead>
<tr>
<th>Type of Fuel Cell</th>
<th>Operating Temperature</th>
<th>Anode and Cathode Reactions</th>
</tr>
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</table>
| Solid Oxide Fuel Cell (SOFC)                      | 500 to 1000°C         | A: $2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$  
C: $O_2 + 4e^- \rightarrow 2O^{2-}$                      |
| Molten Carbonate Fuel Cell (MCFC)                | ~ 650°C               | A: $2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e^-$  
C: $O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$              |
| Phosphoric Acid Fuel Cell (PAFC)                  | ~ 220°C               | A: $2H_2 \rightarrow 4H^+ + 4e^-$  
C: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$                     |
| Alkaline Fuel Cell (AFC)                          | 50 to 200°C           | A: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$  
C: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$                     |
| Proton-Exchange Membrane Fuel Cell (PEMFC)        | 60 to 90°C            | A: $2H_2 \rightarrow 4H^+ + 4e^-$  
C: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$                     |
| Direct Methanol Fuel Cell (DMFC)                  | 60 to 90°C            | A: $CH_3OH + H_2O \rightarrow CO2 + 6H^+ + 6e^-$  
C: $1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$                 |
(a) A simple fuel cell

(b) A typical solid polymer electrolyte fuel cell

Figure 1 Fuel Cell Construction.
Figure 2  Schematic of interfacial structure in a MEA (reproduced from [12]).
CHAPTER 2

ALKALINE MEMBRANE FUEL CELLS USING LIQUID FUELS

2.1 Introduction

Fuel cells running on liquid alcohol fuels are promising candidates for portable applications due to the high energy densities of alcohol and the ease of handling liquid fuels. The use of solid polymer electrolyte further simplifies the design of the fuel cell systems.

These advantages of utilizing liquid alcohol and solid polymer electrolyte are realized in DMFCs. In a DMFC, the system relies on the direct adsorption and oxidation of methanol on platinum-ruthenium-based anodes, and reduction of oxygen on platinum cathodes to convert chemical energy into electrical energy. These chemical reactions occur in an acidic condition present in the fuel cell. The charge carrying protons generated/consumed at the anode/cathode are transported via a PEM, such as Nafion. DMFC technology is a relatively matured technology with state-of-the-art systems exhibiting maximum power density of 70 mW/cm² at 60°C [13] and durability of 2000 hours of operation without significant reduction in power output [14]. However, commercialization of DMFC is hindered by its high cost, particularly due to the cost of platinum-based catalysts and Nafion membranes. The toxicity of methanol with prolonged exposure also complicates the commercialization process of DMFC. Special precautions are necessary in the packaging of the fuel cells, especially the fuel storage to minimize harmful exposure to users.
Direct electro-oxidation of ethanol is another viable option for direct alcohol fuel cell applications [8]. Ethanol, which is less toxic than methanol, has a higher energy density than methanol. These two advantages of ethanol make it a favorable fuel choice than methanol, especially for portable applications.

Present PEM-based DMFC cell design (i.e. the use of platinum-based catalysts and Nafion membranes) is widely adapted in the utilization of ethanol as fuel [15-25]. In a PEM-based direct ethanol fuel cell (DEFC), the chemical equations for the redox reactions are given as,

Anode: \[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \quad E_a^o = 0.084 \text{ V vs. SHE} \quad (1) \]

Cathode: \[ 3\text{O}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow 6\text{H}_2\text{O} \quad E_c^o = 1.229 \text{ V vs. SHE} \quad (2) \]

Overall: \[ \text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 3\text{H}_2\text{O} + 2\text{CO}_2 \quad E_{cell}^o = 1.145 \text{ V} \quad (3) \]

As shown in Equation (1), the complete oxidation of ethanol generates 12 electrons (e\(^-\)). However, the difficulty in breaking the carbon-carbon bond in ethanol often results in incomplete oxidation of ethanol with production of intermediates such as acetaldehyde and acetic acid [8]. The sluggish kinetics of ethanol oxidation at the anode is often overcome by increasing the catalyst loadings and/or by increasing the operating temperature of the fuel cells. Specially fabricated membranes are necessary in fuel cells operating at much higher temperatures [26, 27]. These special membranes and high catalyst loading inherently increase the overall cost of the fuel cell, and limit the potential of PEM-based DEFC as a commercial viable product.
The oxidation of methanol in an aqueous alkaline environment is known to be more facile than in an acidic medium \[28\] and it is also reported that ethanol is more readily oxidized in alkaline solution \[29\]. As demonstrated in AFCs, the ease of alcohol oxidation in alkaline medium allows the use of lower operating temperatures, lower catalyst loadings, and the possibility of using inexpensive catalyst materials. However, electrolyte and electrodes in AFC are susceptible to contamination in the presence of carbon dioxide in the fuel and/or oxidant \[30\]. The use of liquid electrolyte also poses a significant challenge in the packaging of the fuel cell for portable applications.

Fuel cells operating in alkaline environment are receiving renewed interest recently with the advent of new AEMs with properties specifically tailored for fuel cell applications \[31\]. The membrane potentially offers all the advantages of an AFC sans the problems associated with the use of aqueous alkaline electrolyte \[10\]. In an AEM-based DEFC, the chemical equation for the redox reactions at the anode and cathode are as follows,

\[
\text{Anode: } \quad C_2H_5OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^- \quad E^{o}_a = -0.743 \text{ V vs. SHE} \ (4)
\]

\[
\text{Cathode: } \quad 3O_2 + 6H_2O + 12e^- \rightarrow 12OH^- \quad E^{o}_c = 0.401 \text{ V vs. SHE} \ (5)
\]

\[
\text{Overall: } \quad C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2 \quad E^{o}_{cell} = 1.145 \text{ V} \ (6)
\]

From the chemical equations above, it is noted that the complete oxidation of ethanol in alkaline condition will also generate 12 electrons as in acidic fuel cell system. However, counter ionic species in the redox processes are hydroxide anions which are transported from the cathode to the anode via the AEM.
In addition, a key distinction between AEM- and PEM-based fuel cells is the role of water. In an AEM-based system, water becomes a reactant at the cathode and is consumed during the reduction of oxygen at the cathode. At the anode of the AEM-based fuel cell, water is produced during the oxidation of ethanol. This implies that the ethanol fuel does not need to be diluted with water. The possibility of using neat ethanol as fuel could be an added advantage as the size of the fuel storage can be minimized.

Although AEM-based DEFC has a number of attractive attributes, it is still technologically in its infancy and is faced by a variety of challenges that include:

1. membrane instability issue, especially at elevated temperatures
2. poor understanding of the activity and stability behavior of catalyst in alkaline environment, especially non-precious metal catalysts
3. poor conductivity of hydroxide anions in AEM
4. high internal resistance of assembled AMFC
5. new water management strategy to supply water to the cathode

2.1.1 Objectives

In this preliminary study, the potential of using liquid fuel and inexpensive non-platinum catalysts in an AEM-based fuel cell system is examined. The primary objectives are

1. to assess the performance of AMFCs that utilize AEMs and off-the-shelf electrodes, and
(2) to understand the behavior of AMFCs under various operating conditions crucial to the cell performance such as temperature, fuel and oxidant flow rates, and fuel concentration

2.2 Materials

2.2.1 Electrodes and Membranes

Our approach in this preliminary study is to examine the performance of “off-the-shelf” catalysts and membranes. Performances of Hypermec anodic and cathodic electrodes supplied by Acta S.p.A., Italy were investigated. Hypermec electrodes are non-platinum catalysts fabricated using a new templating polymer and transition metal salts [32]. The electrodes are supplied in the form of coated catalysts on nickel foam (anode) and nickel mesh (cathode). The anode catalyst is an alloy that consists of iron, cobalt and nickel, and the cathode catalyst is based on cobalt and iron. The metal loading in the anode and the cathode is 10 wt.% and 3 wt.%, respectively.

AEMs are typically based on quaternary ammonium exchange groups and are widely used in applications such as desalination, purification and electro-dialysis. For fuel cell applications, membranes exhibiting low ionic resistance are highly desirable. In this study, AEM A010, developed by Tokuyama Corporation in Japan, with a membrane thickness of 40 µm and resistance of 0.22 Ω·cm² was used. Ionomer solution A3 (Tokuyama Corporation) with an ionomer content of 5 wt.% was also used in the assembly of the fuel cell to promote the contact between the cathode and the AEM.
2.2.2 Fuel Blends

The fuel blend recommended by the electrode supplier is used in this study. The composition of the fuel blend is as follows,

(a) 10 wt.% ethanol (Sigma-Aldrich, absolute, 200 proof)
(b) 3 wt.% potassium hydroxide (Mallinckrodt Chemicals, pellet, 86 % min)
(c) 0.5 wt.% hydrazine (Sigma-Aldrich, 35 wt.% solution in water)
(d) deionized water

Fuel blend without the addition of hydrazine, and fuel blend without the addition of hydrazine (N$_2$H$_4$) and potassium hydroxide (KOH) were also used in the investigation of the effects of the additives on the cell performance.

2.3 Experimental Procedure

2.3.1 Fuel Cell Assembly and Test Setup

The main components of a miniature fuel cell used in this work are shown in Figure 3. During assembly, a current collector with a 3-pass serpentine flow field (1 mm channel width, 0.5 mm channel depth) was first aligned to the inlet and outlet holes in the end-block. An anodic electrode was then carefully located in the center of the current
collector and a 0.5 mm thick gasket was positioned around the anodic electrode. Following that, an AEM, which had been soaked in 10 wt.% potassium hydroxide solution overnight prior to the assembly, was placed on top of the anodic electrode. A thin layer of ionomer solution A3 was then applied to the top surface of the membrane. A cathodic electrode was aligned to the position of the anodic electrode and placed on top of the membrane. Another gasket was then placed around the cathodic electrode. A cathodic current collector was positioned on top of the cathodic electrode. After positioning an additional end-block, the whole assembly was wench-tightened with bolts and nuts. The assembled miniature AMFC with active area of 1.625 cm$^2$ (0.5 inch × 0.5 inch) is shown in the insert in Figure 3.

The miniature AMFC was supplied with the liquid fuel blend using a Harvard Apparatus Syringe Pump (Model 55-222) assembled with Hamilton Gastight Syringe (Model #1100 or #1010). Air without humidification was supplied via Omega Mass and Volumetric Gas Flow Controller (Model FMA2619A) to the cell. The temperature of the miniature AMFC was regulated with a temperature controller and heating was accomplished by heaters attached to the end-blocks of the fuel cell.

2.3.2 Performance and Electrochemical Characterization

The assembled miniature AMFC was conditioned by operating the fuel cell repeatedly from open circuit condition to maximum current density attainable in the cell. The performance of the fuel cell was then evaluated using Arbin Instruments Portable 4-Station Battery Testing System (Model BT4). Polarization curves were obtained at
various operating parameters, such as fuel flow rate, fuel concentration, air flow rate and operating temperature.

In-situ electrochemical impedance spectroscopy was performed on the assembled miniature AMFC at a potential of 0.5 V using Solotron Electrochemical Interface (Model SI-1278) and Frequency Response Analyzer (Model 1255B). The cathode was set up as the working electrode and the anode functioned as the reference and counter electrodes. The impedance measurement was performed with a frequency sweep from $10^4$ to 0.1 Hz to minimize the drift of operating point at low frequencies ($\sim 0.001$ Hz) and distortion of measurement at high frequencies ($\sim 10^5$ Hz). Five cycles were performed and the steady state data was then extracted for analysis.

### 2.4 Results and Discussion

#### 2.4.1 Cell Performance

The miniature AMFC was supplied with the fuel blend consists of ethanol, hydrazine, potassium hydroxide and water at a flow rate of 0.5 mL/min and non-humidified air at a flow rate of 50 mL/min at standard temperature and pressure (STP). Figure 4 shows the polarization curves obtained for the miniature AMFC at a room temperature of 25°C and at an elevated temperature of 40°C. The open-circuit voltage (OCV) is 0.94 V at 25°C and 0.99 V at 40°C. These OCV values are substantially higher than that observed in PEM-based DEFC, in which OCV of 0.70 V at 30°C is reported [15]. In AEM-based fuel cell in which liquid hydrazine is used as fuel, the OCV
measured ranges from 0.8 to 1.0 V [33]. Therefore, the high OCV values obtained in the miniature AMFC are mainly due to the hydrazine added in the fuel blend.

From Figure 4, it can be seen that a potential drop of about 0.1 V from the OCV value occurred at very low current densities (approximately 5 mA/cm²). The small potential drop at low current densities suggests that the activation-controlled reaction kinetics in the fuel cell was relatively rapid in comparison to the oxidation of alcohol in PEM-based systems. A similar trend is also observed in AEM-based direct hydrazine fuel cell [33]. As such, the cell performance of the miniature AMFC at low current densities is attributed predominantly to the ease of oxidizing hydrazine at lower overpotential.

At current densities higher than 5 mA/cm², a linear variation in voltage with respect to current density was established. The linear relationship is a consequence of the intrinsic ohmic resistance in the fuel cell. The resistance of the miniature AMFC estimated from the slope of V-I curve are 11.4 Ω·cm² and 9.2 Ω·cm² at 25°C and 40°C, respectively. The high resistance of the fuel cell was confirmed with the high-frequency resistance determined from electrochemical impedance spectroscopy performed at 40°C. Figure 5 shows the electrochemical impedance spectrum of the miniature AMFC measured at 40°C. From the plot, the high frequency resistance (HFR) of the cell was determined to be 6.7 Ω·cm². This value is significantly higher than the resistance of 0.22 Ω·cm² in state-of-the-art DMFC. A simple schematic detailing the interfacial structure of the MEA in the assembled miniature AMFC and the corresponding resistance components is shown in Figure 6. With the low membrane resistance and the low electronic resistance in the catalyst layers, the high internal cell resistance is attributed to
the contact resistance at the interfaces in the fuel cell, especially at the electrolyte/electrode interfaces. The polymeric AEM and the metallic anode were pressed together without any interfacial layer. As such, it is likely to contribute to the high overall resistance measured in the fuel cell. The internal resistance of state-of-the-art PEM-based DMFC is reported to be as low as 0.181 \( \Omega \cdot \text{cm}^2 \) [34]. Hence, the internal resistance of the current fuel cell is clearly one of the chief limiting factors to the overall cell performance.

The high resistance of the cell also limited the performance of the miniature AMFC at high current densities. As shown in the polarization curves in Figure 4, a slight deviation from the linear relationship in the voltage-current plot was noted at current densities above 35 mA/cm\(^2\). The absence of a drastic voltage drop at high current densities suggests that the performance of the fuel cell at high current densities is limited by the high internal resistance of the fuel cell than by the mass transport resistance of the reactants.

From the polarization curves in Figure 4, it is noted that the maximum power densities of 16.8 mW/cm\(^2\) at a voltage of 0.448 V and 20.1 mW/cm\(^2\) at a voltage of 0.541 V were obtained at 25°C and 40°C, respectively. The maximum current densities at near short-circuit condition was found to be 54.6 mA/cm\(^2\) and 68.0 mA/cm\(^2\) at 25°C and 40°C, respectively. In essence, the maximum power density achieved in the miniature AMFC was found to be higher than that in DEFC which utilizes PEM and platinum-based catalyst [15]. One of the key factors could be the addition of hydrazine to the fuel used in the current work; and the effect of hydrazine addition will be further examined in the later section.
2.4.2 Effect of Fuel Flow Rate on Cell Performance

The impact of the rates of fuel supply on the cell performance is shown in Figure 7. It is noted that the maximum current density and maximum power density increased with increasing flow rate. However, the maximum current density and maximum power density reached their respective maximum values at a fuel flow rate of 0.5 mL/min.

The mass transport limitation is not pronounced during polarization scan due to the high internal cell resistance. By varying the fuel flow rates, it can be seen that the mass transport limitation can be alleviated with higher flow rates. The mass transport limitation at the anode is in part due to production of carbon dioxide at the anode. Carbon dioxide produced at the anode during operation and its accumulation is known to limit the supply and distribution of fuel to the catalytic sites in DMFC [35]. One of the means of alleviating blockage due to accumulation of CO₂ bubbles is by increasing the flow rate of the fuel, which is evident in the increase in cell performance with increasing fuel flow rate. However, further increase in flow rates resulted in a reduction in limiting current density and maximum power density attained in the fuel cell. This is due to increased fuel crossover associated with increasing fuel flow rate.

Another possible method of minimizing fuel transport limitation at the anode is through the use of wet-proof CL and GDL in the anode. The hydrophobicity in the CL and GDL will facilitate the release of carbon dioxide bubbles. This should be one of the considerations in future development of electrodes for AMFC to minimize transport
limitation and to avoid the detrimental effect of fuel crossover associated with high fuel flow rates.

To date, there is no readily available technique to distinguish the anode overpotential from the cathode overpotential so as to pinpoint the exact causes for reduction in cell performance with different operating conditions, such as increasing fuel flow rates. This can be easily performed in PEM-based systems in which the cathode is fed with hydrogen such that the cathode becomes a dynamic hydrogen reference electrode [36]. However, measuring the anode overpotential in an AEM-based system is not trivial due to the fact that hydroxide ions must be produced at the cathode. Future research is needed to develop a simple reference electrode method for AEM-based fuel cells in order to identify anode and cathode kinetic losses.

A similar effect of the fuel flow rate on performance of the cell was exhibited in 30-minute discharge tests, in which the voltage was measured at a constant current density of 15 mA/cm² (see Figure 8). From the figure, it is also noted that the stability of the miniature AMFC is poor with a voltage drop of 1 mV/min. The membrane stability at elevated temperature is an existing problem for AEMs, which consequently impacts on the overall performance of the miniature AMFC operating at a temperature of 40°C.

### 2.4.3 Effect of Air Flow Rate on Cell Performance

The performance of the miniature AMFC at different air supply rates is depicted in Figure 9. Cell performance, in terms of maximum current density and maximum power density, improved with increasing rate of air supply. An air flow rate of 50
mL/min yielded the best cell performance and subsequently, the performance of the cell deteriorated with further increase in air flow rate. Excess air supply caused the AEM, especially the region near the cathode, to dry up. In general, the ionic conductivity of AEM decreases dramatically with lower water content [37]. Consequently, a decrease in the performance of the fuel cell with a dryer AEM was observed.

The drying out of membrane can be prevented with the use of humidified air. Figure 10 shows the effect of air humidification on the cell performance. From the figure, it is found that the use of humidified air increased the maximum power density from a value of 22.4 mW/cm² at 0.448 V to 25.7 mW/cm² at 0.478 V.

In essence, a better understanding on the state of the membrane and its properties is essential in the advancement of AMFC technology. Monitoring of the membrane resistance by high-frequency resistance (HFR) technique would be helpful to study and understand the state of water in AEMs. Water management in AEM-based fuel cells also emerges as a new challenge due to the fact that water is a reactant for oxygen reduction reaction (ORR) on the cathode and water is possibly electro-osmotically dragged from the cathode to the anode. Thus, as opposed to cathode flooding in PEM-based systems, the cathode in AEM-based system is prone to dry-out. Humidified air feed would be helpful in maintaining water balance in the AMFCs, although this is undesirable in portable applications. Therefore, innovative water management strategies that permit the use of dry air on the cathode should be explored in the future.
2.4.4 Effect of Fuel Concentration and Fuel Type on Cell Performance

As shown in Figure 11, the performance of the fuel cell is influenced by the concentration of ethanol in the fuel blend. Fuel blends with lower ethanol concentration were found to yield better cell performance. Higher ethanol concentration led to higher fuel crossover. As a consequence, the overall performance of the fuel cell is reduced due to depolarization of the crossed over fuel.

The versatility of the AMFC is demonstrated by operating of the fuel cell with fuel blends containing mixture of commercial rum in potassium hydroxide, hydrazine and water. As shown in Figure 12, the cell running on fuel blend with commercial rum performed better than the fuel blend containing 10 wt.% ethanol. The fuel blend with 10 wt.% rum (supplied in 40 vol.%) is equivalent to approximately 4 wt.% ethanol. As discussed earlier, fuel blend with lower ethanol concentration gave better cell performance. The successful power generation using commercial rum reveals the potential of AMFC using bio-ethanol without the need of undergoing stringent purification process.

Methanol is also used as a fuel in the miniature AMFC. Methanol is expected to oxidize much easier than ethanol due to the absence of carbon-carbon bond. However, the performance of the cell operating on methanol fuel was found to be poorer (see Figure 12). This anomaly suggests a possible interaction of the alcohol or its oxidation by-products and the MEA. However, the mechanism of oxidation of methanol and ethanol in AEM is not well established. Therefore, further investigation is necessary to understand the behavior of the fuel cell using different alcohol fuel.
2.4.5 Effect of Fuel Additives

In all the results obtained using the fuel blend of ethanol or methanol with potassium hydroxide, hydrazine and water, it was noted the cell performance is significantly better than that achieved in PEM-based fuel cells in which the fuel consists of diluted ethanol or methanol. Although hydrazine was recommended as an additive in the fuel blend, hydrazine in itself can be used as a fuel and direct oxidation of hydrazine has been demonstrated in AEM-based fuel cells to generate power output [38]. Therefore, fuel blend without the addition of hydrazine was used in the miniature AMFC to examine the effect of hydrazine.

Figure 13 shows the performance of the miniature AMFC using fuel blends with and without the addition of hydrazine. From the plot, it is obvious that the cell performance is significantly reduced without the use of hydrazine. The maximum power density achieved is reduced from 22.4 mW/cm² at 0.488 V by an order of magnitude to 2.14 mW/cm² at 0.251 V when hydrazine is removed from the fuel blend. A significant portion of the cell performance using the original fuel blend is due to the oxidation of hydrazine. This is confirmed in the test in which only hydrazine, potassium hydroxide and water was fed to the miniature AMFC. As shown in Figure 14, the maximum power density achieved with 0.5 wt.% hydrazine and 3 wt.% potassium hydroxide is 20.1 mW/cm² at 0.482 V and the cell performance is very similar to that using original fuel blend.
The potential of using hydrazine as fuel in AMFC was reported by researchers at Daihatsu Motor Co. Ltd. [33]. In their direct hydrazine fuel cell, concentrated hydrazine (0.67M or approximately 2.15 wt.%) in 1M potassium hydroxide was used and a maximum power density of 500 mW/cm² at 80°C was achieved. Although hydrazine is a possible fuel source for AMFC applications, it is mutagenic and its use is strongly discouraged.

Apart from hydrazine, it is also desirable to eliminate the use of potassium hydroxide in the fuel blend. The presence of metal cations (K⁺ in aqueous potassium hydroxide) in AMFC is likely to cause precipitation of carbonate in the electrode and membrane, which impact the durability of the fuel cell. Ultimately, it is highly advantageous that the fuel blend consists of ethanol and water without other additives. Figure 15 shows the performance of the cell using 10 wt.% ethanol in comparison to that using 10 wt.% ethanol and 3 wt.% potassium hydroxide. The performance of the cell was further reduced to a maximum power density of 0.0713 mW/cm² at 0.157 V upon the elimination of potassium hydroxide in the fuel blend. A similar result is also reported in AEM-based DMFC in which addition of sodium hydroxide to methanol aqueous solution was found to be critical in achieving significant cell performance [39].

From the slope of the voltage-current curves in Figure 15, it is estimated that the resistance of the AMFC in the absence of potassium hydroxide is one order of magnitude higher than that exhibited by fuel cell using fuel blend with added potassium hydroxide. Therefore, it is of paramount importance to find an alternative method to maintain the level of hydroxide anions in the AMFC and to preserve the low cell resistance in the absence of potassium hydroxide.
As shown in Figure 16, the performance of the AMFC using 10 wt.% ethanol was found to improve with humidification of air supplied to the cathode. A maximum power density of 0.205 mW/cm\(^2\) at 0.136 V was achieved with the use of humidified air. In the absence of potassium hydroxide, the humidification of oxidant supply becomes of dominant importance.

The performance of the AMFC using diluted ethanol without any additives is significantly lower than that achieved in PEM-based DEFC. Hence, significant improvement in the AMFC and its operation is essential to position the AMFC technology as a viable alternative power source.

2.5 Concluding Remarks

Fuel cells that harness the direct oxidation of liquid fuels are being widely explored as the next energy source for portable power applications. In this work, miniature AMFC using catalysts based on nickel-cobalt-iron system and AEMs were examined. Maximum power densities of 16.8 mW/cm\(^2\) at 0.448 V and 20.6 mW/cm\(^2\) at 0.541 V were achieved at 25°C and 40°C, respectively using a fuel blend that consists of ethanol, potassium hydroxide, hydrazine and water. The cell performance was found to be compromised by the high HFR exhibited by the fuel cell, especially at high current densities.

The mass transport limitation at the anode was demonstrated by varying the fuel flow rates. With higher flow rates, the accumulation of carbon dioxide is alleviated at the anode and the performance of the fuel cell was improved. However, further increase in
flow rate reduced the cell performance due to fuel crossover. The influence of air flow rate on the cell performance was also examined. Excessive air flow caused the AEM to dry up and reduced the cell performance. Air humidification was found to improve the cell performance, especially in the event where potassium hydroxide is eliminated from the fuel supply.

The addition of hydrazine in the fuel blend was found to significantly improve the cell performance due to the ease of oxidation of hydrazine. However, the use of hydrazine as a fuel or an additive is strongly discouraged due to its mutagenicity. The use of potassium hydroxide subjects the AMFC to possible MEA degradation due to carbonation. However, the performance of the fuel cell operating on diluted ethanol without any additives is very poor (maximum power density of 0.0713 mW/cm² at 0.157 V). Hence, significant advancement in the AMFC technology is necessary to increase the cell performance.

From the results presented in this chapter, a number of directions and considerations for future work are identified. In essence, new MEA development is necessary and the following should be considered during the development process,

(1) elimination of additives, including potassium hydroxide, in the operation of AMFC

(2) low HFR value in the assembled AMFC

(3) use of hydrophobicity treatment in CL and GDL to facilitate the release of gaseous by-products

(4) use of humidified oxidant, especially in AMFC operating without potassium hydroxide
Figure 3  An assembled miniature AMFC and its main components.
Figure 4  Performance of miniature AMFC at 25°C and 40°C. (Fuel: 10 wt.% EtOH + 3 wt.% KOH + 0.5 wt.% N₂H₄, F_{Fuel} = 0.5 mL/min, F_{Air} = 50 mL/min)
Figure 5  Electrochemical impedance spectrum of the miniature AMFC.  (T_{cell} = 40°C, Fuel: 10 wt.% EtOH + 3 wt.% KOH + 0.5 wt.% N_2H_4, F_{Fuel} = 0.2 mL/min, F_{Air} = 50 mL/min)
Figure 6  A schematic on the interfacial structure in the assembled MEA and its corresponding resistance components. (R = resistance, C = capacitance, MEM = membrane, CL = catalyst layer, DL = double layer, GDL = gas diffusion layer)
Figure 7  Effect of fuel flow rates on the performance the miniature AMFC. (T_{cell} = 40°C, Fuel: 10 wt.% EtOH + 3 wt.% KOH + 0.5 wt.% N₂H₄, F_{Air} = 50 mL/min)
Figure 8  Effect of fuel flow rates on the performance the miniature AMFC operated at constant current density of 15 mA/cm². (Tcell = 40°C, Fuel: 10 wt.% EtOH + 3 wt.% KOH + 0.5 wt.% N₂H₄, FAir = 50 mL/min)
Figure 9  Effect of flow rate of air supply on the performance of the miniature AMFC. (T_{cell} = 40^\circ C, Fuel: 10 wt.% EtOH + 3 wt.% KOH + 0.5 wt.% N_{2}H_{4}, F_{\text{Fuel}} = 0.5 mL/min)
Figure 10  Effect of humidification of air on the cell performance.  ($T_{\text{cell}} = 40^\circ\text{C},$
Fuel: 10 wt.% EtOH + 3 wt.% KOH + 0.5 wt.% $N_2H_4$, $F_{\text{Fuel}} = 0.5 \text{ mL/min}, F_{\text{Air}} = 50 \text{ mL/min}$)
Figure 11  Effect of fuel concentration on the cell performance.  (T<sub>cell</sub> = 40°C, Fuel: EtOH + 3 wt.% KOH + 0.5 wt.% N₂H₄, F<sub>Fuel</sub> = 0.2 mL/min, F<sub>Air</sub> = 50 mL/min)
Figure 12  Effect of types of fuel on the cell performance. ($T_{\text{cell}} = 40^\circ\text{C}$, $F_{\text{Fuel}} = 0.2$ mL/min, $F_{\text{Air}} = 50$ mL/min)
Figure 13  Performance of miniature AMFC using fuel blend of 10 wt.% EtOH + 3 wt.% KOH with or without N₂H₄. (T_{cell} = 40°C, F_{Fuel} = 0.5 mL/min. F_{Air} = 50 mL/min)
Figure 14 Performance of miniature AMFC using fuel blend of 0.5 wt.% N₂H₄ + 3 wt.% KOH. (T<sub>cell</sub> = 40°C, F<sub>Fuel</sub> = 0.5 mL/min. F<sub>Air</sub> = 50 mL/min)
Figure 15 Performance of miniature AMFC using fuel blend of 10 wt.% EtOH with and without addition of 3 wt.% KOH. (T_{cell} = 40°C, F_{Fuel} = 0.5 mL/min, F_{Air} = 50 mL/min)
Figure 16 Performance of miniature AMFC using fuel blend of 10 wt.% EtOH with dry and fully humidified air at the cathode. ($T_{cell} = 40^\circ C$, $F_{Fuel} = 0.5 \text{ mL/min}$. $F_{Air} = 50 \text{ mL/min}$)
CHAPTER 3
DEVELOPMENT OF A HIGH PERFORMANCE MEA FOR ALKALINE MEMBRANE FUEL CELL OPERATING WITHOUT LIQUID ELECTROLYTE

3.1 Introduction

As pointed out in the previous chapter, the addition of additives to fuel is undesirable for AMFCs. Hydrazine is mutagenic and its use in consumer fuel cell applications is strongly discouraged. The use of potassium hydroxide in AMFCs is also to be avoided as it potentially subjects the fuel cells to carbonation problems experienced in traditional AFCs. In order to fully leverage on the advantage of solid polymer electrolyte in its application to alkaline fuel cells, it is therefore necessary to eliminate the use of potassium hydroxide or any other liquid electrolyte.

The use of solid ionomer in fuel cells operating without liquid electrolyte was first reported by Swette [40]. Using hydrogen and oxygen, the voltage output at a current density of 200 mA/cm² was estimated to be 0.55 V at 40°C, which translates into a power density output of 110 mW/cm². Some of the remarks on the AEMs evaluated in the work include poor stability at temperatures above 60°C, large overall thickness and very high membrane resistance.

Several AEMs have since been developed for all-solid-state AMFC applications in which the use of liquid electrolyte is eliminated during the operation of the fuel cells [41,42]. However, the membranes are often sandwiched between two commercial electrodes developed for PEM-based fuel cells. The fabrication of membrane-electrode
assembly (MEA) specifically for AMFC is still a relative untried technology. High cell resistance is as one of the major challenges to be overcome in the development of MEAs for AMFCs [10].

The fundamental principles of fabrication of MEA for PEMFC and the techniques used to diagnose the performance of the PEMFC are discussed in great details in several review papers [11, 12]. However, there are limited works on the making of MEAs for AMFCs and their characterization reported in the literature.

3.1.1 Current Status on the Fabrication of MEA for AMFC

Varcoe et al. at the University of Surrey (Guildford, United Kingdom) [43] first reported the fabrication of metal-cation-free alkaline MEAs for all-solid-state alkaline fuel cells. In their construct of such MEA, an interfacial layer (polymer loading of 0.97 mg/cm²) was applied to the catalyzed side of commercial electrodes (E-Tek 0.5 mg/cm² Pt/C (20 wt.%)). The interfacial layer is a crossed-linked polymer, in which quaternary ammonium groups bound to the polymer backbone function as the counter ions to the conduction of OH⁻. An AEM was then sandwiched between two of the polymer-coated electrodes and hot pressed together at 100°C and 120 kgf/cm² for 3 min. A maximum power density of 55 mW/cm² at 50°C was attained with 100% RH hydrogen and oxygen circulated at 2 L/min. The lower cell performance in comparison to PEMFC was attributed to high internal cell resistance, which was measured at 1.5 Ω·cm².

Varcoe et al. [41] subsequently reported the incorporation of in-house electron-beam-grafted AEMs in all-solid-state alkaline fuel cells. The anion-exchange polymer
membrane was applied to the anode and cathode (polymer loading was reduced to 0.5 mg/cm²). The electrodes and AEM were not hot-pressed but assembled into fuel cell fixture with a torque of 5.5 Nm. The maximum power densities obtained with hydrogen/oxygen are 90 and 110 mW/cm² at 50 and 60°C respectively. However, the internal cell resistances are 1.0 and 1.1 Ω·cm² at 50 and 60°C respectively. The authors also reported the use of methanol as fuel in a fuel cell with a similar construct, in which power densities of 1.5 and 8.5 mW/cm² at 50 and 80°C were demonstrated.

Varcoe et al. [42] also reported the incorporation of in-house radiation-grafted AEMs in all-solid-state alkaline fuel cells. The anion-exchange polymer membrane was applied to the anode and cathode (polymer loading was reduced to 0.8 mg/cm²). The electrodes and AEM were not hot-pressed but assembled into fuel cell fixture with a torque of 5.5 Nm. The maximum power densities obtained with hydrogen/oxygen at 50°C are 54, 94 and 130 mW/cm² for membranes that are 153, 78 and 51 µm, respectively. The internal cell resistance is 0.9 Ω·cm² at 50°C using the 78 µm-thick membrane. The authors also reported the use of methanol as fuel in a fuel cell with a similar construct, in which power densities of 2.8 mW/cm² at 50°C were demonstrated.

Tamain et al. [44] first reported the mixing of catalyst powder, poly(vinyl benzyl chloride) and ethyl acetate solvent to form a catalyst ink. The ink was sprayed onto GDL and the catalyst-coated GDL was then treated to form alkaline ionomer in the catalyst layer. A maximum power density of 94 mW/cm² was demonstrated on hydrogen/oxygen fuel cell tested at 50°C. A higher power density of 125 mW/cm² was attained using a thinner AEM. However, the internal cell resistance in the assembled AMFCs ranged from 1.5 to 2.0 Ω·cm².
Park et al. [45] used a similar strategy of formulating catalyst ink by mixing catalyst powder, deionized water and 5 wt.% ionomer, prepared using aminated chloromethylated polysulfone in dimethylacetamide. The assembled AMFCs exhibited high internal cell resistance – in the range of $1.5 \text{ }\Omega\cdot\text{cm}^2$ to as high as $17.8 \text{ }\Omega\cdot\text{cm}^2$. The maximum power densities achieved in the fuel cells using hydrogen/air varied from 8 to 30 mW/cm$^2$. The authors also demonstrated comparable cell performance using carbon-supported silver as cathode catalyst in place of expensive platinum catalyst; thereby, highlighting the potential of AMFC using cheaper non-platinum catalysts.

In essence, reasonable performance was demonstrated on AMFCs operating without liquid electrolyte. However, the internal cell resistances of the assembled AMFCs are relatively high, which consequently limit the overall performances of AMFCs.

3.1.2 Objectives

The primary objective in this study is to develop a high performance MEA for an all-solid-state AMFC that operates without the addition of liquid electrolyte. The strategies employed in this work include incorporating ionomer in the formulation of catalyst ink and coating the ink directly onto AEM in attempt to lower the resistance of the fuel cell, increase the catalytic sites available for redox processes, and improve overall cell performance.

In order to facilitate the diagnostic and evaluation of the performance of the AMFCs assembled using the newly developed MEAs, widely studied carbon-supported
platinum catalyst was used in this study. In addition, hydrogen was used as the primary fuel during the characterization process.

3.2 Materials and Experimental Procedure

3.2.1 Fabrication of Catalyst-Coated Membrane or Substrate for AMFC

The procedural steps for the formulation of catalyst ink and the coating of catalyst directly on membrane are summarized as follows. Catalyst ink was prepared by mixing carbon supported platinum (C2-40, 40 wt.% Pt/C by E-Tek), ionomer (AS-4, 5 wt.% by Tokuyama) and 1-propanol (ACS Grade, 99.5 +% by Alfa Aesar). The mixing of the catalyst ink was accomplished by magnetic stirring and ultrasonic agitation. The catalyst ink was then spray-coated on both sides of the AEM. In this study, two types of AEMs were used and their basic properties are summarized in Table 2. Both AEMs have same molecular structure – hydrocarbon backbone with quaternary ammonium side groups [46]. The difference is the thickness of the membrane, in which A901 is 10 µm and A201 is 28 µm. The ionomer AS-4 is also hydrocarbon-based ionic polymer with quaternary ammonium functional groups. The properties of AS-4 are also listed in the table.

The CCMs have an active area of 5 cm², and the catalyst loading on both cathode and anode is 0.4 mg/cm². In this study, CCMs with different ionomer contents (10, 20 and 30 wt.%) were fabricated. The ionomer content is defined as the ratio of the weight of ionomer to the total weight of ionomer and Pt/C catalyst.
In a similar fashion, catalyst-coated substrates were also prepared by spray-coating the catalyst ink directly on 5 cm\(^2\) gas diffusion layers (Toray-H-060 by Toray). The gas diffusion layers were wet-proof with PTFE-treatment and coated with a 30 µm microporous layer (MPL). Figure 17 shows samples of the CCS and CCM fabricated for this study.

### 3.2.2 Assembly of AMFC

Prior to the assembly of AMFC, the fabricated CCM, CCS and AEM were subjected to potassium hydroxide pre-treatment. In the pre-treatment, the CCM, CCS and AEM were soaked in 0.5 M potassium hydroxide for at least 6 hr, rinsed with deionized water, and then soaked in deionized water for at least 12 hr to remove any residual KOH in the components before assembly. The CCM was sandwiched between two pieces of GDLs – wet-proof carbon papers (TGP-H-060 by Toray) coated with 30 µm of MPL. In the case of CCS, the pre-treated AEM was sandwiched between a pair of pre-treated CCS’s. The GDL-CCM-GDL or CCS-AEM-CCS assembly was then placed in a 5 cm\(^2\) graphite fuel cell with single-pass serpentine flow channel, and the cell fixture was tightened with mechanical fasteners to achieve intimate contact among the layers in the test cell. The GDL and the graphite fuel cell used in this study are shown in Figure 18.
3.2.3 Characterization of AMFC

In this developmental study, the AMFC performance was measured at 50°C. As shown in the test setup for performance characterization in Figure 19(a), fully humidified hydrogen was supplied at 0.1 L/min (STP) as fuel and fully humidified air or oxygen was supplied at 0.2 L/min (STP) as oxidant to the cell. The assembled AMFC was preconditioned at 50°C with hydrogen/air by increasing the current density in steps. Steady state voltage at various current density settings was then measured by varying the electronic load in a fuel cell test station (MEDUSA RD-890CR-2050/12550 by Teledyne). The control of operating parameters and the acquisition of data were accomplished with the accompanying software FuelCell for Windows (Version 3.70).

High frequency resistance (HFR) was also recorded with a milliohmmeter (4338B by Agilent Technologies). The resistance value was determined by averaging 5 data points over an interval of 10 s.

Electrochemical characterization of the AMFC was performed using an electrochemical interface coupled with a frequency response analyzer (1287A and 1255B by Solartron). Cyclic voltammetry (CV) was carried out at 25°C by scanning the voltage from 0 to 1 V with a scan rate of 50 mV/s. The test setup for cyclic voltammetry measurement is shown in Figure 19(b). In the setup, fully humidified nitrogen was supplied to the working electrode at 0.1 L/min and fully humidified hydrogen was supplied to the counter electrode, which also acts as the reference electrode, at 0.1 L/min. The CV sweep was performed 5 times and the time-invariant data was then obtained for analysis.
Using the same test setup for cyclic voltammetry measurement, a constant cathode potential of 0.4 V was applied across the electrodes. Steady state crossover current densities due to the crossover hydrogen from the counter electrode to the working electrode were determined at 20, 30, 40 and 50 °C.

3.3 Results and Discussion

3.3.1 Performance of Catalyst-Coated Membrane and Substrate

The CCS’s were assembled with two different types of AEMs for performance characterization - A201 and A9012. A9012 is A901 that has a 3 µm ionomeric binding layer coated on both sides of the membrane. The CCM used in the performance characterization here was prepared on A901.

The hydrogen/oxygen cell performances of AMFCs assembled using CCM and CCS are shown in Figure 20. The HFR measured in CCS/A201 AMFC is 1.681 Ω cm² and the cell performance is poor with a maximum power density of 34.6 mW/cm² at 0.432 V. This is due to poor contact between the electrodes and AEM. The contact was enhanced by using a thinner membrane that was coated with a soft ionomeric layer on both sides of the membrane. The enhancement is evident in the measured HFR value of 0.842 Ω cm². From Figure 20, it is also noted that the cell performance of CCS/A9012 is significantly improved with a maximum power density of 99.5 mW/cm² at 0.311 V.

However, the performance of CCS-based AMFCs is substantially lower than that achieved in CCM-based AMFC. Intimate contact between the catalytic electrode and the
membrane was achieved by directly coating the catalyst ink on the membrane. A superior cell performance of 204 mW/cm$^2$ at 0.318 V was achieved, and the measured HFR value was a mere 0.304 $\Omega \cdot \text{cm}^2$. This HFR value is significantly lower than that reported in the works reviewed in Section 3.1.1, in which catalyst-coated gas diffusion layers were used as the electrodes. This clearly demonstrates the advantage of directly coating catalyst on the membrane for AMFC applications. As such, subsequent AMFCs characterized in this study were assembled using CCMs.

3.3.2 Effect of Ionomer Content on Catalyst Layer

In this study, the CCMs were fabricated by introducing different amount of ionomer in the catalyst layer. The scanning electron micrographs of catalyst layers with ionomer content of 10, 20 and 30 wt.% at low magnification are shown in Figure 21. From the micrographs, it can be noted that the carbon-supported catalysts are evenly distributed in the catalyst layers. Porosity was observed in the catalyst layer and occurred uniformly throughout the catalyst layers. The absence of clusters of carbon particles and of grouping of porosities in the catalyst layer validates the formulation of catalyst ink and the spray coating technique employed in the fabrication of the CCMs.

Figure 22 shows scanning electron micrographs of the catalyst layers at higher magnification. It can be observed that the structure of the catalyst layer is very similar in all the catalyst layers prepared. The structure is predominantly a scaffolding of carbon particles packed together during the spray coating process. Therefore, it is justifiable to conclude that the physical structure of the catalyst layer is mainly attributed to the
physical characteristics of the carbon-supported catalyst. Since the same carbon-supported catalyst was used in all the fabricated CCMs, the thicknesses of the catalyst layers are approximately the same.

The fracture cross-section of the catalyst layer with 20 wt.% ionomer is shown in Figure 23. From the micrograph, the thickness of the catalyst layer can be measured. The average thickness value was determined to be 13 μm. From this thickness value, the level of porosity can be calculated with the known density values of platinum, carbon particle, and ionomer.

The density of carbon (\( \rho_c \)) is ca.1.8 g/cm³ [47], and Vulcan XC-72 carbon is porous, which has a total pore volume (\( V_{pore} \)) of 0.32 cm³/g [48]. Therefore, the density of porous carbon particle, \( \rho_{cp} \) is

\[
\rho_{cp} = \frac{1}{\frac{1}{\rho_c} + V_{pore}} \tag{7}
\]

\[
\rho_{cp} = \frac{1}{\frac{1}{1.8} + 0.32}
\]

\( \rho_{cp} = 1.14 \text{ g/cm}^3 \)

The density of 40 wt.% platinum on porous carbon support, \( \rho_{40\%Pr/C} \) is

\[
\rho_{40\%Pr/C} = \frac{1}{\frac{x_{Pr}}{\rho_{Pr}} + \frac{x_{cp}}{\rho_{cp}}} \tag{8}
\]

\[
\rho_{40\%Pr/C} = \frac{1}{\frac{0.4}{21.46} + \frac{0.6}{1.14}}
\]
\[ \rho_{40\%Pt/C} = 1.84 \text{ g/cm}^3 \]

In the 5cm\(^2\) catalyst layer with 0.4 mg/cm\(^2\) platinum loading, the volume occupied by carbon supported platinum, \(V_{40\%Pt/C}\) is

\[ V_{40\%Pt/C} = \frac{\text{Active Area} \times \frac{\text{Pt Loading}}{0.4}}{\rho_{40\%Pt/C}} \tag{9} \]

\[ V_{40\%Pt/C} = \frac{5 \times 0.4 \times 10^{-3}}{1.84} \]

\[ V_{40\%Pt/C} = 2.72 \times 10^{-3} \text{ cm}^3 \]

The volume occupied by ionomer, \(V_{\text{ionomer}}\) is

\[ V_{\text{ionomer}} = \frac{\text{Active Area} \times \frac{\text{ionomer}}{\text{PtC}} \times \frac{\text{Pt Loading}}{0.4}}{\rho_{\text{ionomer}}} \tag{10} \]

\[ V_{\text{ionomer}} = \frac{5 \times \frac{20}{80} \times 0.4 \times 10^{-3}}{0.97} \]

\[ V_{\text{ionomer}} = 1.29 \times 10^{-3} \text{ cm}^3 \]

The volume of the catalyst layer, \(V_{\text{Catalyst Layer}}\) is

\[ V_{\text{Catalyst Layer}} = \text{Active Area} \times \text{Thickness} \tag{11} \]

\[ V_{\text{Catalyst Layer}} = 5 \times 13 \times 10^{-4} \]

\[ V_{\text{Catalyst Layer}} = 6.50 \times 10^{-3} \text{ cm}^3 \]

Therefore, the porosity level in the catalyst layer can be calculated as follows,

\[ \%\text{porosity} = \frac{V_{\text{Catalyst Layer}} - V_{40\%Pt/C} - V_{\text{ionomer}}}{V_{\text{Catalyst Layer}}} \times 100\% \tag{12} \]
From the average thickness of catalyst layers determined experimentally, the average porosity level in the CCMs was calculated to be 38.3%. This porosity level is expected to be reduced with higher ionomer content as the pores between carbon particles were filled with ionomer. Hence, it is anticipated that the porosity level for CCM with 30 wt.% ionomer to be lower than the calculated average porosity level and that for CCM with 10 wt.% to be higher. In future work, the porosity and surface properties of the catalyst layers can be further examined by using other techniques such as transmission electron microscopy and nitrogen gas absorption.

In essence, the porosity level of 38.3% determined in this work is comparable to the value of 33% calculated for catalyst layer in PEMFC [49]. Physically, the catalyst layers in the CCMs prepared in this study are similar to that prepared for PEMFC. The electrochemical aspect of the catalyst layers prepared will be examined in the next section.

3.3.3 Effect of Ionomer on Electrochemical Active Area

Incorporating ionomer properly in the catalyst layer will also increase platinum utilization. Figure 24 shows cyclic voltammograms (CVs) of the cathode with different ionomer contents. The shaded area in the figure represents the total Coulombic charge associated with hydrogen desorption in the catalyst layer with 10 wt.% ionomer content. Assuming the charge of a smooth platinum surface to be 2.1 C/m², the corresponding
electrochemically active area (ECA) can be calculated as detailed in [50]. The ECA of the CCMs with ionomer content of 10, 20 and 30 wt.% were determined to be 7.56, 13.90 and 11.55 m²/g, respectively. The ECA of the CCMs prepared in this study were much higher than the CCM with ionomer applied to the interface of membrane and catalyst layer (2.13 m²/g), as reported by Rao et al. [51]. The higher ECA in the CCMs fabricated clearly demonstrated the advantage of introducing ionomer in the catalyst layers. However, high ionomer content would result in a larger portion of the carbon-supported catalysts being completely covered/-separated by the ionomer; thereby isolating the catalyst particles and reducing the ECA of platinum available for redox reactions. This is evident in the ECA of CCM with 30 wt.% ionomer being lower than that with 20 wt.% ionomer.

It is also seen that the ECA of the CCM prepared in this work is lower than that for PEMFCs, in which the ECA can be ca. 70 m²/g [52]. This may due to the structural differences in Nafion and AS-4 ionomers, and the interaction between Nafion or AS-4 with the carbon-supported catalysts. Nafion has a non-homogeneous structure with hydrophobic PTFE backbone and hydrophilic ionic side groups. This segregation of phases is absent in the hydrocarbon-based AS-4 ionomer. Therefore, the triple phase boundary in the catalyst layers prepared using AS-4 ionomer was significantly lower and the ECA measured was consequently smaller.

In addition, no surfactant was added to alter the interaction behavior of the ionomer and the catalyst powder. Therefore, further optimization of the MEA for AMFCs may require selecting appropriate organic surfactant in the preparation of catalyst ink.
3.3.4 Effect of Ionomer on Cell Performance

After the cell was fully preconditioned with hydrogen/air at 50°C, the HFR of the fuel cell was measured and found to be 1.417, 0.304 and 0.280 Ω⋅cm² for CCMs with ionomer content of 10 wt.%, 20 wt.% and 30 wt.% respectively. These HFR values are smaller than the range of 0.9 to 17.8 Ω⋅cm² reported in the literatures [43-45]. The benefit of incorporating ionomer in the catalyst layer is evident in the lowering of HFR of the fuel cells with increasing ionomer content.

The effect of ionomer content on ECA was also mirrored on cell performance. As shown in Figure 25 and Figure 26, the best cell performance was attained on CCM with ionomer content of 20 wt.%. In hydrogen/air configuration, a maximum power density of 102 mW/cm² was achieved at 0.256 V. When oxygen was used as the oxidant, the maximum power density was increased to 204 mW/cm² at 0.318 V.

It should be pointed out that the HFR of the fuel cell using hydrogen/oxygen was lower than that with hydrogen/air. Using CCM with ionomer content of 20 wt.%, the HFR of the fuel cell operating on hydrogen/oxygen is 0.218 Ω⋅cm² - a reduction from the value of 0.304 in hydrogen/air. Compressed ambient air, which consists of approximately 380 ppm of carbon dioxide, was used in this study. The carbon dioxide might influence the behavior of the membrane or catalyst layers during the operation of the fuel cell. As such, further work is necessary to examine the effect of carbon dioxide on the performance of the fuel cell.
From Figure 25 and Figure 26, it was observed that the cell potential does not decrease sharply with increasing current density at high current density region. It indicates that hydrogen and oxygen diffusions are not dominating factors in cell performance, but reaction kinetics is. This poor reaction kinetics leads to a sharp cell potential decrease in the low current density region (< 50 mA/cm²). Low reaction kinetics is due to relatively low ECA. Hence, finding a good membrane/ionomer for AMFC to enhance reaction kinetics would be a key for further advancement in the technology.

3.3.5 Effect of Membrane Thickness on Cell Performance

Figure 27 shows the hydrogen/air cell performance with CCMs of different membrane thickness. Thicker membrane A201 yielded a lower maximum power density of 89 mW/cm² at 0.247 V as compared to the value of 102 mW/cm² achieved with thinner membrane A901. As shown in the figure, the performance difference is more pronounced at higher current density. Hence, the performance difference is mainly attributed to the higher resistance of the thicker membrane.

Although CCM with thinner A901 membrane exhibited better cell performance, it is more susceptible to fuel crossover. This was demonstrated in the measurement of OCV, in which the OCV for CCM with thinner A901 membrane is lower due to depolarization of fuel crossover (OCV_{A901} = 1.000 V cf. OCV_{A201} = 1.020 V). The hydrogen crossover occurrence is further examined in the next section.
3.3.6 Effect of Membrane Thickness on Hydrogen Crossover

The hydrogen crossover phenomenon was investigated by measuring the hydrogen crossover current density in the AMFC. The crossover current density was measured by applying a potential of 0.4 V to the cathode, which was supplied with fully humidified nitrogen. The anode, which functions as a counter and reference electrode, was supplied with fully humidified hydrogen.

The hydrogen crossover current densities at different temperatures for membranes A901 and A201 are shown in Figure 28. From the plot, it can be seen that the crossover current densities increased with increasing operating temperatures. The temperature-dependent behavior of hydrogen crossover is related to the diffusion of hydrogen in the membrane. The hydrogen crossover is also dependent on the membrane thickness. The crossover current density measured in A901 is higher than the thicker membrane, A201. At the operating temperature 50°C, the hydrogen crossover current densities for A901 and A201 were determined to be 0.924 mA/cm² and 0.604 mA/cm², respectively. It should be noted that these crossover current densities are relatively low. It is also found that hydrogen crossover is not inverse-proportional to membrane thickness. It indicates that there may be some membrane skin influence on hydrogen crossover.

From the cell performance shown in Figure 27, it is clearly shown that thinner membrane is preferred in AMFC despite its vulnerability to hydrogen crossover, which is generally insignificant in comparison to the gain in overall cell performance at high current densities.
3.4 Concluding Remarks

A high performance MEA has been developed for an all-solid-state AMFC, in which liquid electrolyte is not required during operation of the fuel cell. Direct coating of catalyst on AEM was found to be the better MEA making technique than coating the catalyst on GDLs. The HFR in AMFC assembled using CCS was 0.842 Ω⋅cm$^2$ and that using CCM was 0.304 Ω⋅cm$^2$. This reduction in HFR was also reflected in better cell performance achieved using CCM.

Ionomer content was discovered to impact the ECA values of the MEAs. Low ionomer results in insufficient ionomer coverage in the scaffolding of densely packed carbon-supported catalyst in the catalyst layer; while high ionomer content results in isolation of catalyst particles. An optimum ionomer content of 20 wt.% was found to yield the best ECA value of 13.9 m$^2$/g. This optimum ionomer content was also confirmed in the HFR measurement and cell performance, in which a maximum power density of 102 mW/cm$^2$ at 0.256 V and 204 mW/cm$^2$ at 0.318 V were attained for AMFCs running on hydrogen/air and hydrogen/oxygen, respectively.

The effect of membrane thickness was also investigated in the development of MEAs. Thin AEM was preferred as it gave a low HFR and a high cell performance. Although the hydrogen crossover in thinner AEM was high, the benefits shown in better cell performance of using a thin membrane outweighed this shortcoming.

In this work, it was also realized that carbon dioxide in the oxidant supply has an influence on the HFR of the fuel cell and may impact the overall performance of the fuel cell. The effect of operating parameters on the fuel cell performance was not investigated.
in this developmental study. In the next chapter, these operating parameters will be examined to gain insight on their influence on the cell performance.
Table 2 Basic properties of AEMs and ionomer.

<table>
<thead>
<tr>
<th>Properties</th>
<th>A201</th>
<th>A901</th>
<th>AS-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>28</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Ion-exchange capacitance (mmol/g)</td>
<td>1.7</td>
<td>1.7</td>
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<td>Water content (%)</td>
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</tr>
<tr>
<td>OH− conductivity (mS/cm)</td>
<td>42</td>
<td>38</td>
<td>13</td>
</tr>
</tbody>
</table>
Figure 17 Catalyst-coated substrate (CCS) and catalyst-coated membrane (CCM) for AMFC.
(a) Gas diffusion layer

(b) 1-pass serpentine flow channel in graphite block

(c) Assembled AMFC

Figure 18  An assembled AMFC and its main components.
(a) Cell performance characterization

(b) Cyclic voltammetry and hydrogen crossover measurements

Figure 19  Test setup for various measurement on AMFC.
Figure 20  AMFC performance with MEA assembled via catalyst-coated membrane and catalyst-coated substrate. (T\textsubscript{cell} = 50°C, F\textsubscript{H2} = 0.1 L/min, F\textsubscript{O2} = 0.2 L/min, RH\textsubscript{H2} = 100%, RH\textsubscript{O2} = 100%, p\textsubscript{H2} = p\textsubscript{O2} = 1 atm, absolute)
Figure 21 Scanning electron micrographs of CCMs with different ionomer contents.
Figure 22  Scanning electron micrographs of CCMs with different ionomer contents (higher magnification).
Figure 23  Cross-section of CCM with 20 wt.% ionomer contents.
Figure 24  Cyclic voltammograms (CVs) of the cathode with different ionomer contents. ($T_{cell} = 25^\circ C$, $\nu = 50$ mV/s, $F_{N2} = F_{H2} = 0.1$ L/min, $R_{HN2} = R_{HH2} = 100\%$)
Figure 25  AFMC performance with different ionomer contents in the catalyst layer.

(A901 membrane, \( T_{\text{cell}} = 50^\circ\text{C} \), \( F_{\text{H}_2} = 0.1 \text{ L/min} \), \( F_{\text{air}} = 0.2 \text{ L/min} \), \( \text{RH}_{\text{H}_2} = \text{RH}_{\text{air}} = 100\% \), \( p_{\text{H}_2} = p_{\text{air}} = 1 \text{ atm, absolute} \)
Figure 26  AFMC performance with different ionomer contents in the catalyst layer.

(A901 membrane, \( T_{\text{cell}} = 50^\circ\text{C} \), \( F_{\text{H}_2} = 0.1 \text{ L/min} \), \( F_{\text{O}_2} = 0.2 \text{ L/min} \), \( \text{RH}_{\text{H}_2} = \text{RH}_{\text{O}_2} = 100\% \), \( p_{\text{H}_2} = p_{\text{O}_2} = 1 \text{ atm, absolute} \)
Figure 27  Effect of membrane thickness on cell performance. (A901 vs. A201 membrane, 20 wt.% ionomer. $T_{\text{cell}} = 50^\circ \text{C}$, $F_{\text{H}_2} = 0.1 \text{ L/min}$, $F_{\text{air}} = 0.2 \text{ L/min}$, $R_{\text{H}_2} = R_{\text{air}} = 100\%$, $p_{\text{H}_2} = p_{\text{air}} = 1 \text{ atm, absolute}$)
Figure 28  Effect of membrane thickness on hydrogen crossover current density.
(A901 vs. A201 membrane, 20 wt.% ionomer. \( F_{H_2} = 0.1 \) L/min, \( F_{N_2} = 0.2 \) L/min, \( R_{H_2} = R_{N_2} = 100\% \), \( p_{H_2} = p_{N_2} = 1 \) atm, absolute)
CHAPTER 4
EFFECTS OF OPERATING CONDITIONS ON THE PERFORMANCE OF
ALKALINE MEMBRANE FUEL CELL

4.1 Introduction

The AMFC technology is still in its infancy stage with considerable effort dedicated to the development of new AEMs based on different polymer systems in recent years [53 - 57]. The current work, together with that reviewed in Section 3.1.1, represents another major research effort in integrating newly developed AEMs and other materials in the making of MEAs for AMFC applications. Collectively, reasonable power output has been demonstrated in AMFC systems; with the maximum power densities of 204 mW/cm² and 102 mW/cm² using hydrogen/oxygen and hydrogen/air reported in the previous chapter being the highest power output in the literature at the time of finding.

The developmental work has primarily focused on getting maximum cell performance using the new materials and devising new processing procedures to make MEAs for the AMFCs. Limited works have examined the performance of the fuel cells under different operating conditions. The understanding of the behavior of the AMFCs operating under various conditions could lead to further advancement of the technology.

One of the major concerns in the operating of a traditional AFC is the presence of carbon dioxide in the fuel or oxidant supply. Although the carbonation problem is avoided with the removal of metal cations in the use of AEMs in AMFCs, the influence
of carbon dioxide on the performance of AMFCs should still be evaluated. This is because neutralization of the AEMs was found to occur within a short period of exposure to ambient air [46]. It was reported that absorption of carbon dioxide gas to wet AEMs occurs readily and the hydroxide ions in the AEMs were replaced by carbonate and bicarbonate anions (\(\text{CO}_3^{2-}\) and \(\text{HCO}_3^{-}\)). The mobility of bicarbonate anion is much lower than that for hydroxide anion. Consequently, the ionic conductivity in the AEMs can be reduced by a factor of four when the hydroxide-form AEMs are changed into bicarbonate form. In the case of Tokuyama membrane A201, the ionic conductivity in hydroxide-exchanged form is 42 mS/cm while that in bicarbonate-exchanged form is reduced to 10 mS/cm.

The pH values of aqueous solution of hydroxide, carbonate and bicarbonate are approximately 13.5, 11.6 and 8.3 respectively. Therefore, the replacement of hydroxide anions by carbonate and bicarbonate anions in the AEMs could lower the alkalinity in the AMFCs. This lower pH value compromises the kinetic advantage of facile electrochemical reactions in alkaline environment.

The decrease in ionic conductivity and alkalinity due to the replacement of hydroxide by carbonate and bicarbonate anions could lead to a reduction in cell performance. Hence, the performance of AMFCs operating with the presence of carbon dioxide should be examined.

The concentration of carbonate and bicarbonate anions in the AMFCs can be reduced with the hydroxide anions produced during the operation of the fuel cells. In the oxygen reduction reaction at the cathode, hydroxide anions are produced as follows,

\[
\text{Cathode: } \quad \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad (13)
\]
The generation of hydroxide anions at the cathode replaces the carbonate anions; and the carbonate content in AEM was observed to decrease during continuous operation of AMFC [58]. This phenomenon of reducing carbonate content in the AEM by hydroxide anions generated during the operation of the fuel cell is termed self-purging.

4.1.1 Objectives

The first part of this work is to study the influence of conditioning and operating parameters on the cell performance. In particular, the following topics are investigated:

(1) effect of pre-treatment and conditioning on cell performance

(2) effect of types of oxidant on cell performance

With the potential issues caused by the presence of carbon dioxide, the investigation was focused primarily on the role of carbon dioxide and making adjustment to the pre-treatment and conditioning parameters to minimize the effect of carbon dioxide on the fuel cell performance.

With a better understanding on the effect of conditioning and operating parameters on the cell performance, the second part of this work was carried out in attempts to further improve the fuel cell performance. In the previous chapters, the ionomer contents of 10, 20 and 30 wt.% was investigated. In this chapter, the ionomer contents was narrowed down to 15, 20 and 25 wt.% to determine the optimum ionomer content for best performance of the AMFC.
4.2 Materials and Experimental Procedure

The same procedure, as described in Section 3.2.1, was followed in the preparation of CCMs used in this work. In the making of the new batch of CCMs, catalyst inks with different ionomer contents were prepared. During the fabrication process, the ink temperature was maintained at 40-50°C to achieve more uniform ink. From the previous work, it was noted that 20 wt.% ionomer content gave the best cell performance. Therefore, the range of ionomer content was narrowed down to 15, 20 and 25 wt.% in this work to determine the optimum ionomer content.

In addition, a new AEM (A20X2) was also evaluated in this work. A20X2 is a developmental membrane, which has a thickness of 28 µm, an ion-exchange capacity of 1.8 mmol/g, and an electrical resistance of 0.2 Ω·cm². As for A9012, A20X2 is coated with ionomer layer on both sides of the membrane.

As described in Chapter 3, the prepared CCMs were treated in potassium hydroxide prior to cell assembly and testing. The CCMs were soaked in 0.5 M potassium hydroxide for at least 6 hours. They were then rinsed with de-ionized water and subsequently soaked in de-ionized water for at least 12 hours. In this work, the CCMs were soaked in air-tight containers filled with nitrogen-saturated de-ionized water to minimize the exposure of the CCMs to carbon dioxide from the environment. For single cell testing, the CCM was sandwiched between 2 wet-proof carbon papers (TGP-H-060) and assembled in the 5 cm² test cell.
The assembled AMFCs were characterized in the same manner as detailed in Section 3.2.3. In some cases, pure air with carbon dioxide content less than 1 ppm was used as the oxidant for the fuel cells.

4.3 Results and Discussion

4.3.1 Effect of Pre-Treatment on Cell Performance

Upon assembly of the AMFC, the temperature of the fuel cell was raised to 50°C, and hydrogen and oxygen were supplied at a flow rate of 0.1 L/min and 0.2 L/min, respectively. A low constant voltage was then applied across the electrodes, and the current density and HFR of the fuel cell was measured. Figure 29 shows the current density and the HFR with respect to time when the AMFC was held at a low constant voltage. The initial HFR of the fuel cells with CCM pre-treated with potassium hydroxide and untreated CCM were 0.296 Ω⋅cm² and 0.448 Ω⋅cm², respectively. Wet AEM and ionomer has a high selectivity for carbonate and bicarbonate anions, and the hydroxide anions were reported to be completely replaced by carbonate and bicarbonate anions after 30 min of exposure to ambient air [46]. Due to poor mobility of carbonate and bicarbonate anions, the untreated CCM exhibited higher resistance. The pre-treatment with potassium hydroxide restored the hydroxide concentration in the CCM. As a consequence, a lower HFR of the assembled AMFC was measured.

The untreated CCM was soaked in de-ionized water prior to assembly to eliminate the effect of hydration on the ionic conductivity in the CCM. From the figure, the
resistance value of the AMFC with CCM that did not undergo any potassium hydroxide pre-treatment was found to decrease with increasing period of time, and reached a stable value after approximately 6 minutes. The reduction in resistance value was attributed to the self-purging effect, in which residual carbonate and/or bicarbonate anions in the AEM and ionomer were replaced by mobile hydroxide anions generated from the oxygen reduction reaction.

The starting HFR value of the AMFC with pre-treated CCM was lower, indicating the beneficial effect of potassium hydroxide pre-treatment to remove residual carbonate and bicarbonate anions in the MEA. The self-purging phenomenon was less obvious as evident in the instantaneous attainment of the low HFR upon operating of the fuel cell. In addition, the cell’s current density reached a stable value much faster than that without potassium hydroxide pre-treatment. It should be pointed out that the current density achieved in the AMFC with potassium hydroxide pre-treatment is lower than that without pre-treatment is due to the constant voltage at which the measurement was taken. The AMFC with potassium hydroxide pre-treatment was held at a higher constant voltage than that without any pre-treatment.

The potassium hydroxide pre-treatment of CCM was also found to improve the cell performance. Figure 30 shows the performance difference between AMFCs assembled with CCM pre-treated in potassium hydroxide and CCM that did not undergo any pre-treatment. It can be noted that the maximum power density of the cell was increased from 217 mW/cm² at 0.494 V to 365 mW/cm² at 0.397 V when the CCM was subjected to potassium hydroxide pre-treatment. The benefit of the pre-treatment was
also reflected in the HFR values. It was found that the HFR of the treated CCM was reduced from 0.172 to 0.152 $\Omega \cdot \text{cm}^2$.

Both AEM and ionomer solution were supplied in hydroxide-exchanged form. However, the AEMs were reported to be susceptible to neutralization due to absorption of carbon dioxide from the ambient air [46]. Therefore, the hydroxide anions in the AEMs, especially in the ionomer solution, were replaced by carbonate and/or bicarbonate anions during storage. This test shows the importance of the pre-treatment of the CCM in potassium hydroxide solution to restore the hydroxide species in the membrane and the ionomer in the catalyst layer prior to fuel cell testing. For subsequent work, the potassium hydroxide pre-treatment is employed as a required standard procedure prior to assembly and testing of AMFCs.

4.3.2 Effect of Cell Conditioning on Cell Performance

For the work reported in the previous chapter, the assembled AMFC was conditioned in hydrogen/air prior to the characterization of cell performance. The presence of carbon dioxide in ambient air could have limited the overall performance of the AMFC. In addition, the higher oxygen concentration in pure oxygen supply could be advantageous in the conditioning process. Therefore, the AMFC was conditioned using hydrogen/oxygen in this work to examine the effect conditioning the cell using pure oxygen.

The performance attained with AMFC conditioned using hydrogen/oxygen is compared to that achieved with AMFC conditioned using hydrogen/air in the previous
work; and the polarization curves are shown in Figure 31. The maximum power densities of hydrogen/oxygen AMFC conditioned with oxygen and ambient air are 365 mW/cm² at 0.397 V and 204 mW/cm² at 0.318 V, respectively. Another advantageous gain with oxygen conditioning is the reduction in the HFR of the AMFC, in which the resistance value was reduced from 0.218 Ω⋅cm² to 0.152 Ω⋅cm².

From these results, the detrimental effect of carbon dioxide on the AMFC performance was again confirmed. It was also demonstrated that this detrimental effect can be minimized by using pure oxygen during the cell conditioning. As such, pure oxidants such as pure oxygen and pure air are necessary to extract the best power output from the AMFCs. The use of pure air during the operation of the fuel cells may be beneficial and will be examined in the next section.

In hydrogen AMFCs, the carbon dioxide in the fuel cells is introduced via the oxidant or the environment. The carbon dioxide issue can be a major challenge when ethanol or methanol is used as fuel. Carbon dioxide is produced during complete oxidation of ethanol or methanol. This additional source of carbon dioxide could further worsen the carbon dioxide problem in AMFCs using alcohol fuel. Hence, development of AEM and ionomer is still a crucial element in advancing the AMFC technology. In essence, there is a need to develop AEM and ionomer that are tolerant to carbon dioxide and have a higher selectivity for hydroxide anions over other anions.
4.3.3 Effect of Types of Oxidant on Cell Performance

The performances of the AMFCs using three different types of oxidant are shown in Figure 32. The maximum power densities obtained for the AMFC using pure oxygen, pure air and ambient air as oxidant are summarized in Table 3 and the corresponding values of the HFR measured are also listed in the table. In essence, the use of pure oxidant (pure oxygen and pure air) yielded better performance than ambient air, which contains carbon dioxide.

From the polarization curves in Figure 32, the oxygen gain due to a higher oxygen concentration with the use of pure oxygen is evident in the improved performance of hydrogen/pure oxygen AMFC over that supplied with hydrogen/pure air. The difference in polarization curve of the two increased with increasing current density, indicating mass transport limitation at the cathode. The mass transport limitation could be caused by the electrode structure or flooding in the cathode due to the supply of fully humidified oxidant. Additional work in the future could include the use of helox (oxygen with helium) to elucidate if the mass transport limitation is caused by poor oxygen diffusion in water-saturated or dry electrode. The information gathered will be very useful in devising a better water management strategy in the AMFCs.

The oxygen concentrations in both pure air and ambient air are the same. Therefore, the mass transport limitation for oxygen in the cathode is very similar for both types of air. As a consequence, the maximum current densities achieved in AMFCs operating with pure air and ambient air are approximately the same at 800 mA/cm². However, an interesting phenomenon was observed when comparing the polarization
curves for AMFCs using pure air and ambient air at low current densities. It was noted that the voltage attained at low current densities differed by a large amount even though both types of air have the same oxygen concentration. It is clear that the kinetic loss in AMFC using ambient air is much higher than that using pure air. The formation of carbonate and bicarbonate anions from the carbon dioxide present in ambient air lowered the alkalinity in the AMFC. The oxygen reduction reaction is known to be sensitive to pH value, with faster reaction kinetics at higher pH values. Therefore, a significant kinetic loss was observed when ambient air was used as the oxidant in the AMFC.

Several works have been performed to study the oxygen reduction reaction in aqueous alkaline media as reviewed by Spendelow et al. [59]. However, there are very limited understanding on the reduction of oxygen in solid alkaline membranes and its dependence on pH values. Similarly, the hydrogen oxidation reaction in AMFCs is not well understood. It is of paramount interests to determine the kinetic loss due pH changes and to separate the kinetic loss at the anode and the cathode.

4.3.4 Effect of Temperature on Cell Performance

The polarization curves for the AMFC operating at different temperatures are shown in Figure 33, and the key performance parameters are summarized in Table 4. As expected, the maximum power density of the AMFC increased with increasing operating temperature. From Figure 33, it was noted that the slope of the linear portion of the polarization curve decreased with increasing operating temperature. This is due to the increase in conductivity in the membrane at higher operating temperatures. The increase
in ionic conductivity was also reflected in the HFR values of the AMFC, in which the lowest HFR was measured at 40°C. It was also found that the HFR values at 40°C and 50°C were very similar. Therefore, no further reduction in HFR was expected at temperature higher than 50°C. At higher temperature, the cell performance could be compromised by poor stability of the ionomer and AEM. In this work, the maximum temperature at which the AMFCs operated is limited to 50°C to minimize the stability issues in the ionomer and AEMs. This temperature is lower than that used in Nafion-based PEMFCs, which are generally operated at a temperature of 80°C. Hence, it is critical to develop new ionomer and AEMs, which has a tolerance to higher operating temperatures to generate better cell performance at possibly a higher efficiency.

From Figure 33, it was also observed that the maximum current density achieved in the cell increased with increasing operating temperature. The diffusion of the fuel and oxidant were enhanced at higher temperatures. Therefore, the mass transport of the hydrogen and oxygen was improved.

### 4.3.5 Effect of Ionomer Content on Cell Performance

In this study, the effect of ionomer content on the cell performance was examined again by narrowing the range of ionomer contents from 15 to 25 wt.%. The same method as that discussed in the previous chapter was used in the preparation of the CCMs used in this work. The hydrogen/oxygen cell performance of the AMFCs assembled with CCMs of ionomer contents of 15, 20 and 25 wt.% is shown in Figure 34, and that for hydrogen/air is shown in Figure 35. The corresponding maximum power densities
obtained and the HFR resistances of the fuel cells are summarized in Table 5. From the polarization curves, it was confirmed that the ionomer content of 20 wt.% is the optimum amount of ionomer for the AMFC performance. The maximum power density achieved in AMFC using hydrogen/oxygen in this current study is 365 mW/cm², which is the highest reported in the literature.

The HFR values of the current batch of CCMs were found to be lower than that prepared in Chapter 3. For an ionomer content of 20 wt.%, the HFR values of the new CCM was 0.152 Ω⋅cm² as compared to 0.218 Ω⋅cm² achieved in the earlier CCM. The reduction in HFR value was attributed to the strategy employed in this current study to minimize exposure carbon dioxide.

Figure 36 show the scanning electron micrographs of the CCMs prepared. As expected, the CCMs were characterized by homogenous catalyst layer with even distribution of carbon-supported catalysts and porosities. Similar packing of carbon particles was also observed at higher magnification, as shown in Figure 37. From the fracture cross-section in Figure 38, the average thickness of the current batch of CCMs prepared was determined to be 14 µm, which is higher than the 13 µm thickness reported for the previous batch of CCMs. The porosity level was subsequently determined as 42.7%. This porosity level was decreased with further increase in ionomer content (such as 25 wt.%). The reduction in porosity level limited the mass transport of fuel and oxidant and was evident in the lower maximum current density achieved in CCM with 25 wt.% ionomer content.

The CVs of the cathodes with ionomer contents of 15, 20 and 25 wt.% are shown in Figure 39. From the CV curves, the ECAs were determined to be 13.5, 17.9 and 13.4
m²/g for CCM with ionomer content of 15, 20 and 25 wt.%, respectively. The ionomer content of 20 wt.% was again confirmed as the optimum ionomer content giving the maximum ECA. The best ECA obtained in this batch of CCMs was found to be higher than that reported for the earlier batch of CCMs, in which the best CCM with an ionomer content of 20 wt.% exhibited an ECA of 13.90 m²/g. The higher ECA achieved in the current work was attributed to better quality in catalyst ink prepared with increasing experience in the preparation process.

However, the ECA measured in this work is still significantly lower than that obtained in PEMFCs. Nafion, widely used in PEMFCs, has a non-homogenous structure with hydrophobic and hydrophilic clusters that inherently increases the triple phase boundary, where electrolyte, gas, and electrically connected catalyst meet. The ionomer used in the making of CCMs for AMFC is a hydrocarbon with quaternary ammonium groups, in which phase segregation in the polymer is absent. Therefore, increasing ECA is a key and big challenge for a high performance AMFC.

Figure 40 shows the results of the electrochemical impedance spectroscopy performed on CCMs with various ionomer contents. The horizontal distance as depicted in the figure is proportional to the charge transfer resistance. It can be seen that the charge transfer resistance for CCM with an ionomer content of 20 wt.% is the smallest among the CCMs prepared in this study.
4.3.6 Effect of Types of Membrane on Cell Performance

The hydrogen/oxygen cell performances of AMFCs using different types of membranes are shown in Figure 41. In addition, the AMFCs were also tested using hydrogen/pure air and the polarization curves are depicted in Figure 42. The maximum power densities and the HFR values of the AMFC are summarized in Table 6. It was noted that thin A901 membrane yielded the best cell performance over thicker membrane A201. The higher resistance of a thicker membrane is evident in the higher HFR measured in the AMFC with A201 membrane. The performance of the AMFCs using membranes with thin layer of ionomer coatings was found to be compromised by higher HFR values. The coatings increased the interfaces in the MEAs and significantly increased the HFR values in the cell.

The self-purging effect in the AMFCs with different membranes was also investigated. Figure 43 shows the current density and HFR variation with time during constant voltage operation. It noted that the self-purging in A9012 and A20X2 were very similar but generally slower than in A901. The self purging was relatively independent on the thickness of the membrane but it was slower due to the presence of ionomer layers in both A9012 and A20X2. These binding layers represent additional resistance to the movement of hydroxide anions and limited the replacement of carbonate and/or bicarbonate ions by hydroxide anions.

From the results above, it is clear that thin membrane without additional ionomer layers is preferred in the fabrication of CCMs by direct coating of catalyst on the membrane.
4.4 Concluding Remarks

The performance of AMFCs was found to be influenced by various conditioning and operating parameters. Pre-treatment of CCM with potassium hydroxide was found to be a critical step in restoring the hydroxide level in the MEA. The replacement of carbonate and bicarbonate anions by hydroxide anion decreased the HFR of the AMFC and enhanced the performance of the fuel cell. The self-purging occurred much faster in the pre-treated CCM and a stable low HFR value was attained almost instantaneously. The performance of the AMFCs was also dependent on the type of oxidant used in the conditioning of the cell. Pure oxygen minimized the carbon dioxide contamination in the AMFC and consequently yielded a better cell performance. The performance of AMFC conditioned using ambient air was compromised with a higher HFR due to absorbed carbon dioxide from the air. The cell performance increased with increasing operating temperature as higher operating temperature was found to increase ionic conductivity, improve mass transport and enhance the reaction kinetics. However, the maximum operating temperature was limited to 50°C with concern about the stability of the AEMs at temperatures beyond that.

With a better understanding on parameters affecting the performance of AMFCs, a new batch of CCMs was developed and characterized. The ionomer content of 20 wt.% was confirmed as the optimum amount of ionomer in the catalyst layer for AMFC applications. The CCM with 20 wt.% was found to have the largest ECA at 17.9 m²/g and smallest charge transfer resistance. Consequently, the cell performance was
improved - maximum power densities were \( 365 \text{ mW/cm}^2 \) at \( 0.397 \text{ V} \) for hydrogen/oxygen and \( 213 \text{ mW/cm}^2 \) at \( 0.409 \text{ V} \) for hydrogen/pure air. These maximum power density values are the highest in the literature to date.
### Table 3 Maximum power density and HFR of AMFC with different oxidant.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure oxygen</td>
<td>365 (at 0.397 V)</td>
<td>0.152</td>
</tr>
<tr>
<td>Pure air</td>
<td>213 (at 0.409 V)</td>
<td>0.190</td>
</tr>
<tr>
<td>Ambient air</td>
<td>133 (at 0.237 V)</td>
<td>0.300</td>
</tr>
</tbody>
</table>
Table 4  Maximum power density and HFR of AMFC at different operating temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>178 (at 0.370 V)</td>
<td>0.213</td>
</tr>
<tr>
<td>40</td>
<td>264 (at 0.366 V)</td>
<td>0.195</td>
</tr>
<tr>
<td>50</td>
<td>325 (at 0.338 V)</td>
<td>0.197</td>
</tr>
</tbody>
</table>
Table 5  Maximum power density and HFR of AMFC with different ionomer contents and operating with hydrogen/oxygen and hydrogen/air.

<table>
<thead>
<tr>
<th>Ionomer Content (wt.%)</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂/O₂</td>
<td>H₂/Air</td>
</tr>
<tr>
<td>15</td>
<td>230 (at 0.383 V)</td>
<td>97 (at 0.243 V)</td>
</tr>
<tr>
<td>20</td>
<td>365 (at 0.397 V)</td>
<td>133 (at 0.237 V)</td>
</tr>
<tr>
<td>25</td>
<td>180 (at 0.450 V)</td>
<td>84 (at 0.262 V)</td>
</tr>
</tbody>
</table>
Table 6  Maximum power density and HFR of AMFC with different membranes and operating with hydrogen/oxygen and hydrogen/air.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂/O₂</td>
<td>H₂/Pure Air</td>
</tr>
<tr>
<td>A901</td>
<td>365 (at 0.397 V)</td>
<td>213 (at 0.409 V)</td>
</tr>
<tr>
<td>A9012</td>
<td>179 (at 0.406 V)</td>
<td>134 (at 0.372 V)</td>
</tr>
<tr>
<td>A201</td>
<td>153 (at 0.425 V)</td>
<td>-</td>
</tr>
<tr>
<td>A20X2</td>
<td>209 (at 0.402 V)</td>
<td>176 (at 0.399 V)</td>
</tr>
</tbody>
</table>
Figure 29  Self-purging effect on MEA pre-treated with KOH and without any pre-treatment in KOH. (Membrane A901, 20 wt.% ionomer, $T_{\text{cell}} = 50^\circ$C, $F_{\text{H}_2} = 0.1$ L/min, $F_{\text{O}_2} = 0.2$ L/min, $RH_\text{H}_2 = RH_\text{O}_2 = 100\%$, $p_{\text{H}_2} = p_{\text{O}_2} = 1$ atm, absolute)
Figure 30 Effect of pre-treatment of MEA using KOH on cell performance. (20 wt.% ionomer, $T_{cell} = 50^\circ\text{C}$, $F_{H_2} = 0.1 \text{ L/min}$, $F_{O_2} = 0.2 \text{ L/min}$, $R_{H_2} = R_{O_2} = 100\%$, $p_{H_2} = p_{O_2} = 1 \text{ atm, absolute}$)
Figure 31 Effect of conditioning using O2 and air on cell performance. (20 wt.% ionomer, $T_{\text{cell}} = 50^\circ \text{C}$, $F_{\text{H2}} = 0.1 \text{ L/min}$, $F_{\text{O2}} = 0.2 \text{ L/min}$, $RH_{\text{H2}} = RH_{\text{O2}} = 100\%$, $p_{\text{H2}} = p_{\text{O2}} = 1 \text{ atm, absolute}$)
Figure 32  Effect of different oxidants on cell performance. (Membrane A901, 20 wt.% ionomer, $T_{\text{cell}} = 50^\circ\text{C}$, $F_{\text{H}_2} = 0.1 \text{ L/min}$, $F_{\text{oxidant}} = 0.2 \text{ L/min}$, $R_{\text{H}_2} = R_{\text{oxidant}} = 100\%$, $p_{\text{H}_2} = p_{\text{oxidant}} = 1 \text{ atm, absolute}$)
Figure 33  Effect of operating temperatures on cell performance. (20 wt.% ionomer, \( F_{H2} = 0.1 \) L/min, \( F_{O2} = 0.2 \) L/min, \( RH_{H2} = RH_{O2} = 100\% \), \( p_{H2} = p_{O2} = 1 \) atm, absolute)
Figure 34  Effect of ionomer content on cell performance. (Membrane A901, T_cell = 50°C, F_H2 = 0.1 L/min, F_O2 = 0.2 L/min, RH_H2 = RH_O2 = 100%, p_H2 = p_O2 = 1 atm, absolute)
Figure 35  Effect of ionomer content on cell performance. (Membrane A901, \( T_{\text{cell}} = 50^\circ C \), \( F_{\text{H}_2} = 0.1 \) L/min, \( F_{\text{air}} = 0.2 \) L/min, \( \text{RH}_{\text{H}_2} = \text{RH}_{\text{air}} = 100\% \), \( p_{\text{H}_2} = p_{\text{air}} = 1 \) atm, absolute)
Figure 36  Scanning electron micrographs of CCMs with different ionomer contents.
Figure 37 Scanning electron micrographs of CCMs with different ionomer contents (higher magnification).
Figure 38  Cross-section of CCM with 30 wt.% ionomer contents.
Figure 39 Effect of ionomer content on cyclic voltammetry. (Membrane A901, T\textsubscript{cell} = 50\degree C, F\textsubscript{H2} = 0.1 L/min, F\textsubscript{N2} = 0.2 L/min, RH\textsubscript{H2} = RH\textsubscript{N2} = 100\%, p\textsubscript{H2} = p\textsubscript{N2} = 1 atm, absolute)
Figure 40 Effect of ionomer content on electrochemical impedance spectroscopy.

(Membrane A901, $T_{\text{cell}} = 50^\circ\text{C}$, $F_{\text{H}_2} = 0.1$ L/min, $F_{\text{air}} = 0.2$ L/min, $RH_{\text{H}_2} = RH_{\text{air}} = 100\%$, $p_{\text{H}_2} = p_{\text{air}} = 1$ atm, absolute)
Figure 41 Effect of different types of membrane on H2/O2 cell performance. (20 wt.% ionomer, T_{cell} = 50°C, F_{H2} = 0.1 L/min, F_{O2} = 0.2 L/min, RH_{H2} = RH_{O2} = 100%, p_{H2} = p_{O2} = 1 atm, absolute)
Figure 42 Effect of different types of membrane on H2/air cell performance. (20 wt.% ionomer, T_{cell} = 50^\circ C, F_{H2} = 0.1 L/min, F_{air} = 0.2 L/min, R_{H2} = R_{air} = 100\%, p_{H2} = p_{air} = 1 atm, absolute)
Figure 43  Self-purging effect on MEA with different membranes.  (Ionomer Content = 20 wt.% ionomer, $T_{\text{cell}} = 50^\circ\text{C}$, $F_{\text{H}_2} = 0.1$ L/min, $F_{\text{O}_2} = 0.2$ L/min, $R_{\text{H}_2} = RH_{\text{O}_2} = 100\%$, $p_{\text{H}_2} = p_{\text{O}_2} = 1$ atm, absolute)
5.1 Introduction

As mentioned earlier, significant efforts have been directed into the development of AEMs and MEAs for AMFC applications. In these developmental works, the primary priority has been getting reasonable performance from the AMFCs. Significant breakthrough in cell performance has been achieved, in which maximum power densities of 365 mW/cm$^2$ and 213 mW/cm$^2$ for hydrogen/oxygen and hydrogen/pure air AMFC have been demonstrated.

Apart from cell performance, another important factor considered in determining the commercial viability of a fuel cell is its durability. As pointed out earlier, the durability of the current state-of-the-art DMFC was demonstrated to exceed 2000 hours [14]. Hence, comparable durability in AMFCs is necessary to challenge PEM-based fuel cells as potential alternative power sources.

As AMFC technology is still a relatively new technology, there are very limited amount of information on the durability of AMFCs available in the literature. To date, there are very few reports that discuss the durability of AMFCs. In their AMFC using methanol and air, Varcoe et al. [43] reported a degradation rate of 95 µV/hr and the cell resistance was found to be 5.9 Ω-cm$^2$ without noticeable increase in a medium-term durability test at a temperature of 50°C and a constant current discharge of 0.1 A. No
significant loss in performance over a 6-day period was also reported in AMFC using methanol and air by Scott et al. [60]. In the work carried out for hydrogen AMFCs [41 - 45], there is no mention on the stability of the fuel cells. Hence, very little is known about the stability of AMFCs and factors that affect the stability of the fuel cells.

5.1.1 Objectives

This work was carried out to gain a better understanding on the behavior of AMFCs during prolonged testing. In particular, the objective of this work is to identify the factors that affect the stability of the AMFCs.

5.2 Materials and Experimental Procedure

The CCMs developed in the previous two chapters were used in the stability tests. After characterizing the performance of the AMFCs, a constant current density was maintained and the resulting voltage was measured with time. The HFR values of the fuel cells were also recorded using the milliohmmeter.
5.3 Results and Discussion

5.3.1 Effect of Ionomer Content on Stability

Figure 44 shows the influence of ionomer content on the stability of the hydrogen/oxygen AMFCs at a constant current density of 120 mA/cm². From the figure, it was noted that the HFR increased with time and the voltage decreased with time. The rate of HFR increment and the rate of voltage reduction were estimated from Figure 44, and the values are summarized in Table 7. It was found that the overall stability of the fuel cells was affected by the ionomer content in the catalyst layers. At low ionomer content of 15 wt.%, the fuel cell degraded much faster with a voltage reduction rate of 497 mV/hr and the cell’s HFR increased at a rate of 0.857 Ω·cm²/hr. Higher ionomer contents (20 and 25 wt.%) appeared to promote the longevity of the fuel cells, in which the cells continued to generate power for more than 100 hours. AMFC with 25 wt.% ionomer content was also found to be more stable than that with 20 wt.% ionomer content. The poor stability of the AMFCs is likely due to the degradation of ionomer in the catalyst layers. The fuel cell stability can be improved with the use of higher ionomer content. However, there exists a trade-off as AMFCs with higher ionomer content are limited by poorer mass transport and reduced cell performance.

In general, the ionomer has sufficient chemical stability. However, fuel cell is an electrochemical device and the electrochemical stability of the ionomer is unknown. In addition, the ionomer is in contact with catalyst which may further change the behavior of the ionomer. Ex-situ characterization of the stability of ionomer in electrochemical
environment could provide useful data in analyzing the stability of AMFCs. However, in-situ examination of the ionomer in the assembled fuel cells may have greater impact in characterizing the ionomer degradation and devising strategy to stabilize the fuel cell performance with increasing time. Transparent fuel cell has been used to study liquid water and ice formation in the catalyst layer [49]. Similar test setup can be used to perform in-situ spectroscopy on the catalyst layer.

5.3.2 Effect of Types of Membrane on Stability

The stabilities of AMFCs using different types of membrane were determined using hydrogen/pure air at a constant current density of 120 mA/cm$^2$. The voltage and HFR variations with continuous operation of the AMFCs are shown in Figure 45. From the plots, the rate of voltage reduction and rate of HFR increment was estimated and presented in Table 8. It was noted that the use of thicker membrane (A20X2) did not improve the stability of the fuel cell. However, the coating of ionomer layers on the membranes (A20X2 and A9012) was found to improve the cell stability. The rates of voltage reduction for AMFCs with the coating of interfacial ionomer layer were one order of magnitude lower than that without the coating. This is indicative that the stability of the ionomer at the electrode/electrolyte interface may be instrumental in determining the overall stability of the AMFC.
5.3.3 Effect of Carbon Dioxide in Oxidant on Stability

Although carbon dioxide in oxidant has been reported to have a detrimental impact on the cell performance in terms of lower power output and higher HFR values, there was no conclusive evidence to suggest that it adversely affects the fuel cells’ stability. As shown in Figure 46, the AMFC operating on ambient air as oxidant was found to degrade slower than that using pure air at a constant current density of 120 mA/cm². The voltage reduction rate of 11 mV/hr and HFR increment rate of 37.2 mΩ⋅cm²/hr were estimated for stability test using ambient air and that for pure air were 73.5 mV/hr and 109 mΩ⋅cm²/hr, respectively. Therefore, the presence of carbonate and bicarbonate anions in the MEAs did not accelerate the degradation of the cell performance. With the use of pure air, the concentration of carbonate and bicarbonate anions was reduced and concentration of hydroxide anion was increased. Therefore, the hydroxide anion might contribute to the accelerated performance degradation of AMFC using pure air. The effect of hydroxide anion on the cell stability can be examined by performing the stability tests at different current densities.

5.3.4 Effect of Operating Current Density on Stability

The stability of AMFCs was found to be dependent on the current density level at which the stability test was conducted. Figure 47 shows the voltage and HFR with respect to time for stability tests conducted at 120 mA/cm² and 600 mA/cm². At higher current density, the voltage was found to decrease at a faster rate of 23.2 mV/hr than the
rate of 1.39 mV/hr at lower current density. In addition, the increase in HFR was faster at a rate of 8.06 mΩ⋅cm²/hr (cf. 1.41 mΩ⋅cm²/hr at lower current density).

Degradation of quaternary amine functional groups (-N+(CH₃)₃) in anion exchange resins subjected to strong alkali and high temperature was reported [61]. When the AMFC was operated at high current densities, the hydroxide anion concentration increased, especially at the cathode. With the elevated operating temperature of the AMFC, the loss of anion-exchange functional group in the ionomer at the cathode is very likely.

5.3.5 Characterization of an Aged AMFC

CV was performed on the AMFC at the end of the stability test. The CV plot together with that obtained in as-assembled condition was shown in Figure 48. The ECA was calculated from the plot and it was found that the ECA of the cell was reduced from 10.21 to 0.23 m²/g after the stability test. Since platinum is stable in alkaline medium, the loss of triple phase boundary was attributed to the loss of ionomer in the catalyst layers.

Raman spectroscopy was performed on the catalyst layers of fresh CCM and aged CCM. The carbon:ionomer ratios were determined by comparing the peak intensities of the Raman spectra obtained. A preliminary analysis of the data shows that the carbon:ionomer peak ratio reduced from 1:1 to 1:0.85 after ageing [62]. This reduction confirmed the loss of ionomer in the catalyst layer after stability test.
Attempts to restore the cell performance after aging in a stability test were made by subjecting failed CCM to potassium hydroxide treatment. Figure 49 shows the polarization curves of an AMFC in as-assembled condition, and after potassium hydroxide treatment. From the figure, it is clear that only a limited portion of the cell performance was restored – approximately 11% of the original maximum power density of 317 mW/cm². The linear slope of the polarization curve showed a much higher cell resistance in the aged AMFC. The original HFR of the AMFC is 0.177 Ω·cm² and the value was increased to 2.054 Ω·cm² after aging. The subsequent treatment with potassium hydroxide did not reduce the HFR of the cell. Therefore, the loss of conductivity and performance were not recoverable with potassium hydroxide treatment. It is affirmed that the loss of conductivity is more than the loss of hydroxide anions. The anion-exchange functional groups in the catalyst layer and possibly in the AEM were be lost during the stability tests.

5.3.6 Effect of Prolonged Storage of CCM on Cell Performance

Figure 50 shows the cell performance of AMFCs assembled with CCMs that was stored 1 day after fabrication and that which was stored in ambient condition after 4 months after fabrication. The maximum power density determined from the polarization curves and the HFR of the fuel cells are summarized in Table 9. It was noted that the performance of the CCM after prolonged storage was poorer than that tested 1 day after fabrication. This is due to possible degradation of ionomer in the catalyst layer. As pointed out earlier, the ionomer has sufficient chemical stability in absence of platinum
catalyst. However, the degradation of the ionomer may be accelerated in the presence of platinum catalyst. More work is needed in determining the properties of ionomer in simulated condition experienced in a fuel cell.

5.3.7 Water Transport during Stability Test

From the various plots of voltage versus time obtained in the stability tests, drops in voltage that were subsequently recovered were observed. These recoverable drops in voltage were possibly due to flooding in the electrode. The water transport behavior in the AMFCs, which is critical in the operating of the fuel cells, has not been reported in the literature. During the stability tests, attempts were made to gain some insights on the water transport in the AMFCs.

In the stability tests, water was collected at the anode exhaust, which is the sum of water from the humidified hydrogen, water produced at the anode and water transported from the cathode to the anode. Therefore, the water transported from the cathode to the anode can be determined as follows,

\[ n_{\text{transport}} = n_{\text{out}} - n_{\text{in}} - n_{\text{produced}} \]  \hspace{0.2cm} (14)

where \( n_{\text{out}} \), \( n_{\text{in}} \) and \( n_{\text{produced}} \) are the number of moles of water in the inlet, outlet and that produced at the anode, respectively. The net water transport coefficient is defined as the number of mole of water transported from the cathode to the anode per mole of hydroxide produced. Mathematically,

\[ \alpha = \frac{n_{\text{transport}}}{n_{\text{OH}^-}} \]  \hspace{0.2cm} (15)
Figure 51 shows the values of net water transport coefficient at different current densities measured during stability tests. It was noted that water was transported from anode to the cathode during the fuel cell operation. Therefore, the cathode was more vulnerable to flooding. The transport of water between the electrodes is dependent on diffusion, hydraulic permeation and electro-osmotic drag. At higher current density, the transport of water from cathode to the anode by electro-osmotic drag was more pronounced; thereby resulted in a bigger net water transport coefficient.

The work presented here is a preliminary investigation on the water transport in AMFCs. To gain a better understanding of the water transport and its management in AMFCs, more detailed experimental works are necessary.

5.4 Concluding Remarks

The stability of AMFCs was significantly lower than that in PEMFCs. The AMFC stability was found to be dependent on the amount of ionomer in the catalyst layers. Higher ionomer content was determined to improve the stability of the fuel cell. The poor stability was attributed to degradation of ionomer in the catalyst layer, especially near the electrode/electrolyte interfaces. This is evident in the improved cell stability in MEAs in which thin layers of ionomer were coated on the AEMs. Carbon dioxide in the oxidant supply was found to have no detrimental bearing on the fuel cell’s stability. However, the cell degradation was significantly accelerated when the fuel cell was operated at higher current density.
The ECA of aged MEA was determined to be $0.23 \text{ m}^2/\text{g}$ – a significant reduction from the original value of $10.21 \text{ m}^2/\text{g}$. The loss of ECA was due to the loss of ionomer in the catalyst layer. Attempts to restore the cell performance by potassium hydroxide treatment were unsuccessful. Hence, the loss of ionomer could be more than just the loss of anionic species; indicating probable loss of ionic side groups. The stability of the ionomer during storage of CCMs was also found to be poor. AMFC assembled with CCM stored for 4-month period suffered a reduction in cell performance.

Preliminary investigation on the water transport behavior in the AMFC was carried out during the stability tests. In essence, water was found to be transported from the anode to the cathode that may cause potential flooding at the cathode.
Table 7 Rates of voltage reduction and HFR increment during stability test of AMFCs with different ionomer content.

<table>
<thead>
<tr>
<th>Ionomer Content (wt.%)</th>
<th>Rate of Voltage Reduction (mV/hr)</th>
<th>Rate of HFR Increment (mΩ-cm²/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>495</td>
<td>857</td>
</tr>
<tr>
<td>20</td>
<td>1.39</td>
<td>1.41</td>
</tr>
<tr>
<td>25</td>
<td>0.986</td>
<td>0.725</td>
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</tbody>
</table>
Table 8  Rates of voltage reduction and HFR increment during stability test of AMFCs with different types of membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Rate of Voltage Reduction (mV/hr)</th>
<th>Rate of HFR Increment (mΩ·cm²/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A901</td>
<td>73.5</td>
<td>109</td>
</tr>
<tr>
<td>A9012</td>
<td>7.31</td>
<td>4.31</td>
</tr>
<tr>
<td>A20X2</td>
<td>8.23</td>
<td>9.01</td>
</tr>
</tbody>
</table>
Table 9 Maximum power density and HFR of AMFC with CCMs after 1-day and 4-month storage in ambient air.

<table>
<thead>
<tr>
<th>CCM Storage</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>365 (at 0.397 V)</td>
<td>0.152</td>
</tr>
<tr>
<td>4 months</td>
<td>196 (at 0.445 V)</td>
<td>0.183</td>
</tr>
</tbody>
</table>
Figure 44  Effect of ionomer content (15 wt.%, 20 and 25 wt.%) on stability of AMFC. (Membrane A901, $T_{cell} = 50^\circ$C, $F_{H2} = 0.1$ L/min, $F_{O2} = 0.2$ L/min, $RH_{H2} = RH_{O2} = 100\%$, $p_{H2} = p_{O2} = 1$ atm, absolute)
Figure 45  Effect of types of membrane on stability of AMFC. (T_{cell} = 50\degree C, F_{H2} = 0.1 L/min, F_{pure air} = 0.2 L/min, RH_{H2} = RH_{pure air} = 100\%, p_{H2} = p_{pure air} = 1 \text{ atm, absolute})
Figure 46  Stability of AMFC using pure air and ambient air. (Membrane A901, $T_{\text{cell}} = 50^\circ\text{C}$, $F_{\text{H}_2} = 0.1$ L/min, $F_{\text{oxygen}} = 0.2$ L/min, $R_{\text{H}_2} = R_{\text{oxygen}} = 100\%$, $p_{\text{H}_2} = p_{\text{oxygen}} = 1$ atm, absolute)
Figure 47  Stability of AMFC at different current densities. (Membrane A901, $T_{cell} = 50^\circ C$, $F_{H_2} = 0.1$ L/min, $F_{O_2} = 0.2$ L/min, $R_{H_2} = R_{O_2} = 100\%$, $p_{H_2} = p_{O_2} = 1$ atm, absolute)
Figure 48  CV for AMFC in as-assembled condition and after aging in stability testing (Membrane A901, $T_{\text{cell}} = 50^\circ\text{C}$, $F_{\text{H}_2} = 0.1 \text{ L/min}$, $F_{\text{N}_2} = 0.2 \text{ L/min}$, $RH_{\text{H}_2} = RH_{\text{N}_2} = 100\%$, $p_{\text{H}_2} = p_{\text{N}_2} = 1 \text{ atm}$, absolute)
Figure 49  Cell performance prior to stability test and after stability test and KOH treatment (Membrane A901, T_{cell} = 50^\circ C, F_{H_2} = 0.1 \text{ L/min}, F_{O_2} = 0.2 \text{ L/min}, RH_{O_2} = RH_{H_2} = 100\%, p_{H_2} = p_{O_2} = 1 \text{ atm, absolute})
Figure 50  Cell performance of AMFC assembled with as-prepared CCM and CCM that was stored for a period of 4 months. (Membrane A901, T_{cell} = 50^\circ C, F_{H2} = 0.1 L/min, F_{O2} = 0.2 L/min, RH_{H2} = RH_{O2} = 100\%, p_{H2} = p_{O2} = 1 \text{ atm, absolute})
Figure 51 Net water transport coefficient at different operating current densities.

(Membrane A901, $T_{\text{cell}} = 50^\circ \text{C}$, $F_{\text{H}_2} = 0.1 \text{ mL/min}$, $F_{\text{O}_2} = 0.2 \text{ L/min}$, $RH_{\text{H}_2} = RH_{\text{O}_2} = 100\%$, $p_{\text{H}_2} = p_{\text{O}_2} = 1 \text{ atm, absolute}$)
CHAPTER 6
DEVELOPMENT OF MEA FOR ALKALINE MEMBRANE FUEL CELL
OPERATING ON LIQUID ALCOHOL FUEL

6.1 Introduction

Liquid alcohol is an attractive fuel choice for fuel cells, especially for fuel cells in portable applications. The potential of using liquid alcohol in AMFC was demonstrated in one of the earlier works in this project using commercially available components. Since then, a number of works have been reported by other researchers on the development of MEA for direct alcohol AMFCs using ethanol or methanol as fuel.

6.1.1 Current State-of-the-Art of Direct Alcohol AMFC

Yu et al. [63] reported the use of AEM for DMFC applications. Carbon supported platinum (60 wt.% Pt) and PTFE solution (as a binding agent) was used in the preparation of catalyst layers. 2 M methanol in 1 M sodium hydroxide was fed to the anode at a rate of 60.6 mL/min and air was supplied to the cathode at a flow rate of 2 L/min. A maximum power density of approximately 11 mW/cm² was achieved at 60°C. The performance of the cell was found to be improved by sandwiching a catalyzed AEM (directly chemical deposited with platinum) between the electrodes [64].

Hou et al. [65] reported the use of AEM with commercially purchased electrodes developed for PEM-based fuel cells. 2 mg/cm² PtRu/C and 1 mg/cm² Pt/C were used as
the anode and cathode respectively. The assembled fuel cell was supplied with 2 M ethanol and 2 M potassium hydroxide to the anode and oxygen to the cathode. The maximum power densities of 49 and 61 mW/cm² were obtained at 75 and 90°C, respectively. A maximum power density of 31 mW/cm² was attained at 90°C using methanol as a fuel in a similar fuel cell [66].

Fujiwara et al. [67] reported the use of AEM, and unsupported Pt and PtRu black catalysts in the fabrication of MEAs for DEFC applications. The catalyst layers consist of 3.0 mg/cm² catalyst and 5 wt.% ionomer. The cell performance of the AEM-based DEFC operating with 1 M ethanol was poor at room temperature. The maximum current density attainable in the fuel cell was 8 mA/cm². The poor performance was attributed to insufficient hydroxide conductivity. Addition of potassium hydroxide was found to be necessary to provide the required conductivity of hydroxide. With the addition of 0.5 M potassium hydroxide, the maximum power density was reported to increase to a value of 58 mW/cm².

Varcoe et al. [41] first demonstrated the use of methanol as a fuel for AMFC without the need for adding aqueous metal hydroxide. 4 mg/cm² PtRu and 4 mg/cm² Pt black on carbon cloths were used as anode and cathode, respectively in the fuel cell. The AMFC was operated with 2 M methanol at a flow rate of 10 mL/min and humidified oxygen at 2 L/min. The maximum power densities achieved at 50 and 80°C were 1.5 and 8.5 mW/cm². The better performance of the fuel cell at 80°C was achieved in part with the use of back pressures at both electrodes. The performance at 50°C was further improved with the use of thinner AEM, in which a maximum power density of 2.8 mW/cm² was attained [42]. Apart from methanol, Varcoe et al. also utilized liquid fuels,
such as ethanol and ethylene glycol, in their AEM-based direct alcohol fuel cells at an elevated temperature of 50°C [68]. The maximum power densities obtained for ethanol, methanol and ethylene glycol were 2.09, 2.16 and 1.99 mW/cm², respectively.

Bunazawa et al. [69] also reported the use methanol as a fuel in AEM-based DMFC. In the making of the MEAs, ionomer was introduced in the catalyst ink and the resulting ink was spray-coated directly on the membrane. PtRu/C (30 wt.% Pt and 23.3 wt.% Ru) was used for the anode and Pt/C (46.6 wt.% Pt) was used for the cathode. The catalyst loading for the anode was 0.75 mg/cm² of Pt and 0.58 mg/cm² of Ru and that for the cathode was 1.40 mg/cm² Pt. It was reported that an ionomer content of 45.4 wt.% gave the best cell performance. At a temperature of 80°C, a maximum power density of 7.57 mW/cm² was demonstrated using a supply of 1M methanol at a flow rate of 5 mL/min and humidified oxygen at a flow rate of 100 mL/min.

Scott et al. [60] demonstrated the use of aqueous solution of 1 M methanol in a direct methanol AMFC. The anode and cathode catalyst layers were prepared using 60 wt.% PtRu/C and 60 wt.% Pt/C, respectively. Nafion solution was used as a binder in the catalyst layers and the platinum loadings for both electrodes were 1 mg/cm². The assembled fuel cell was supplied with methanol at a flow rate of 2.78 mL/min and non-humidified air at a rate of 0.4 L/min. The cell exhibited a maximum power density of 6 mW/cm² at 60°C. With the use of oxygen, the maximum power density was reported as 16 mW/cm².

In essence, the performance of direct alcohol AMFC using ethanol as fuel is lower than that achieved in PEM-based systems. In the case of using methanol as fuel, the performance obtained in AEM-based systems is far below that attained in DMFC.
6.1.2 Objectives

The objective of this work is to develop a MEA for direct alcohol AMFC operating on alcohol fuel without the need for addition of aqueous metal hydroxide. The emphasis of the work will be examining the use of ethanol as a fuel in the MEAs developed.

6.2 Materials and Experimental Procedure

6.2.1 Fabrication of Catalyst-Coated Membrane for Direct Alcohol AMFC

The steps for making MEAs for direct alcohol AMFC operating on liquid alcohol fuel are very similar to that detailed in Section 3.2.1. The anode and cathode catalysts used in the study are carbon-supported platinum-ruthenium (HP 80 wt.% Pt:Ru (1:1) by E-Tek) and carbon-supported platinum (HP 80 wt.% Pt by E-Tek), respectively.

From the earlier work, it was found that structure of the catalyst layers are predominantly determined by the physical structure of the carbon particles. Hence, the same volumetric ratio of ionomer to carbon particle was used in calculating the ionomer content required in the formulation of catalyst ink for alcohol-fed AMFCs in this work. The densities of the metal, porous carbon and calculated values of different weight ratios of carbon-supported catalysts are summarized in Table 10.
From the results obtained, the ionomer content of 20 wt.% gave the best cell performance. By keeping the equivalent volumetric ratio of ionomer to carbon-supported platinum constant, the ionomer content required for cathode using 80 wt.% Pt/C can be calculated as follows,

\[
\frac{V_{\text{ionomer}}}{V_{40\% \text{Pt/C}}} = \frac{m_{\text{ionomer}} / \rho_{\text{ionomer}}}{m_{40\% \text{Pt/C}} / \rho_{40\% \text{Pt/C}}} = \frac{m_{\text{ionomer}} / \rho_{\text{ionomer}}}{m_{80\% \text{Pt/C}} / \rho_{80\% \text{Pt/C}}} \tag{17}
\]

\[
\frac{m_{\text{ionomer}}}{m_{40\% \text{Pt/C}} \times \rho_{40\% \text{Pt/C}}} = \frac{m_{\text{ionomer}}}{m_{80\% \text{Pt/C}} \times \rho_{80\% \text{Pt/C}}}
\]

\[
\frac{m_{\text{ionomer}}}{m_{80\% \text{Pt/C}}} = \frac{20}{80} \times \frac{1.84}{4.71}
\]

\[
\frac{m_{\text{ionomer}}}{m_{80\% \text{Pt/C}}} = 8.9 \quad \frac{9.2}{91.1}
\]

For anode using 80 wt.% PtRu/C,

\[
\text{Error! Objects cannot be created from editing field codes.}
\]

\[
\frac{m_{\text{ionomer}}}{m_{80\% \text{PtRu/C}}} = \frac{20}{80} \times \frac{1.84}{4.51}
\]

\[
\frac{m_{\text{ionomer}}}{m_{80\% \text{PtRu/C}}} = \frac{9.2}{90.8}
\]

From the calculations based on equivalent volumetric ratios, the ionomer contents required for the cathode and anode are 8.9 wt.% and 9.2 wt.%, respectively. For this work, the ionomer content for cathode was fixed at 8 wt.% and three different ionomer
contents (6, 8 and 10 wt.%) were evaluated for anode. The loading of PtRu/C in the anode was 4 mg/cm² and that of Pt/C in the cathode was 2 mg/cm².

6.2.2 Testing of Direct Alcohol AMFC

The CCMs were subjected to the same potassium hydroxide treatment as detailed in Chapter 4. Wet-proof carbon paper (Toray-H060) with 30 µm MPL was used as cathode GDL. Wet-proof carbon paper (Toray-H060) with MPL or untreated carbon paper without MPL was used as anode GDL. The whole assembly was secured in the 5 cm² graphite fuel cell.

The AMFC was delivered with 1 M ethanol or 1 M methanol at a flow rate of 1 mL/min. Fully humidified oxygen or ambient air was supplied to the cathode at a flow rate of 0.2 L/min. The fuel cell was conditioned at 50°C by step-increasing current densities to the maximum current density achievable. Prior to obtaining the polarization curve, the HFR of the fuel cell was measured and steady state voltages at different current density settings were then recorded.

6.3 Results and Discussion

6.3.1 Effect of Types of GDL on Cell Performance

Different GDLs, wet-proof carbon paper and untreated carbon paper, were evaluated in the testing of AMFC using ethanol as fuel and oxygen as an oxidant. The
HFR exhibited by the AMFCs assembled with wet-proof and untreated carbon papers are 0.330 and 0.332Ω⋅cm², respectively. The similarity in the measured HFR values was expected, as the wet-proofing of the GDL did not alter the electrical and ionic characteristic of the MEA.

Figure 52 shows the performance of the fuel cells using wet-proof and untreated carbon paper. The maximum power densities of AMFC using treated GDL (6.248 mW/cm² at 0.246 V) was better than that using untreated GDL 5.240 mW/cm² at 0.213 V). From Figure 52, it was noted that the use of wet-proof GDLs enhanced the mass transport and resulting in a higher maximum current density. Therefore, the use of wet-proof GDLs in direct alcohol AMFC is strongly recommended.

6.3.2 Effect of Ionomer Content in Anode on Cell Performance

Figure 53 and Figure 54 show the polarization curves of AMFCs operating with ethanol/oxygen and ethanol/air, respectively. The maximum power densities determined from the polarization curves and the corresponding HFR values of the ethanol AMFCs are summarized in Table 11. The average OCV values of the AMFC using ethanol/oxygen and ethanol/air were approximately 0.70 and 0.69 V, respectively. With the application of a very low current density (1.6 to 2.0 mA/cm²), a large voltage drop was observed in ethanol/air AMFC. This is due to lower oxygen concentration in the air supplied to the cathode. The performance gain with the use of pure oxygen was also demonstrated in higher current densities, and a higher maximum power density was obtained in ethanol/oxygen AMFC. The maximum power densities achieved in
ethanol/oxygen and ethanol/air were 6.482 mW/cm² at 0.222 V and 3.380 mW/cm² at 0.130 V, respectively. The ionomer content of 6 to 8 wt.% in the anode appeared to give the best cell performance. However, more work is required to affirm the optimal ionomer content in the anode, and future work should include the investigation of ionomer content in the cathode on the cell performance.

The maximum power density values achieved in this study are higher than the value of 2.09 mW/cm² demonstrated on an ethanol/oxygen AMFC [68]. However, the performance of the direct ethanol AMFC is still lower than that demonstrated in PEM-based systems, in which maximum power densities ranged from 26 to 110 mW/cm² was achieved at higher operating temperatures [15-25]. As such, significant advancement in the direct ethanol AMFC technology is still necessary.

It was observed that the HFR values of direct ethanol AMFCs were substantially higher than that obtained for hydrogen AMFCs. Again, the use of ambient air was found to increase the HFR values. However, the increase was not as significant as that measured for hydrogen AMFCs. In direct ethanol AMFCs, the neutralization of ionomer and AEM was caused by carbon dioxide introduced via the oxidant and that produced upon complete oxidation of ethanol at the anode. This again highlights the need for carbon dioxide tolerant AEM and ionomer. Varcoe et al. [58] recently reported a hydrogen/air AMFC that was carbon dioxide tolerant. The performance of the fuel cell was found to be better when tested with AEM in carbonate-form than in hydroxide-form. However, no data was reported for direct alcohol AMFCs.

The presence of carbon dioxide in the cathode was found to limit the performance of hydrogen AMFCs in the previous work. The generation of carbon dioxide as by-
product in the oxidation of ethanol at the anode may further compromise the cell performance. In this study, no attempt was made to differentiate the performance reduction due to carbon dioxide in the oxidant at the cathode and carbon dioxide in by-products of the oxidation of ethanol at the anode. Future work in identifying the performance loss due to presence of carbon dioxide in the anode and cathode may helps in determining the viability of using direct oxidation of ethanol in AMFC applications.

6.3.3 Effect of Potassium Hydroxide on Cell Performance

The beneficial effect of adding potassium hydroxide to ethanol fuel is evident in Figure 55. The maximum power density was significantly improved from 5.240 mW/cm² at 0.213 V to 22.02 mW/cm² at 0.367 V with the potassium hydroxide addition. Another major improvement with the addition of potassium hydroxide is the drastic reduction in HFR – HFR of the fuel cell was 0.0663 Ω⋅cm² with the addition of potassium hydroxide as opposed to 0.332 Ω⋅cm² without the potassium hydroxide addition. This is indicative of the insufficient hydroxide conductivity in the AEMs. The poor hydroxide conductivity in the AEM is a major obstacle in further improvement of the cell performance. Therefore, the success of AMFCs could be dependent on the development of AEM and ionomer with a high selectivity for hydroxide anions to maintain adequate ionic conductivity in the fuel cells. In addition, adding potassium hydroxide may also benefit anode kinetics.
6.3.4 Comparison of Ethanol and Methanol as Fuel in AMFC

Figure 56 shows the performance of the AMFCs operating on 1 M ethanol and 1 M methanol as fuel. The maximum power densities and HFR values of the fuel cells are summarized in Table 12. The performance of the direct methanol AMFC was poorer in comparison to direct ethanol AMFC. In the study of using methanol, ethanol and ethylene glycol as fuel, Varcoe et al. reported that methanol gave the highest maximum power density at 2.16 mW/cm² [68]. A thick membrane (60 µm) was used in the Varcoe’s AMFC while a thinner membrane (10 µm) was used in the current work. The thinner membrane is more susceptible to fuel crossover. Therefore, poisoning of cathode by adsorbed methanol (crossover from anode to cathode) or carbon monoxide (an intermediate from the oxidation of methanol) was more severe in the current AMFC with the use of methanol. The oxidation of ethanol is generally incomplete, with acetic acid reported as the major oxidation product [67]. Consequently, the poisoning of cathode was less severe and the kinetic loss was less significant with the use of ethanol as fuel.

Figure 57 shows the fuel crossover in AMFCs using ethanol or methanol as fuel. It was also noted that the crossover of methanol occurred more readily than ethanol. The limiting crossover current densities for ethanol and methanol were determined to be 80 and 166 mA/cm², respectively. It has been reported that ethanol shows a lower permeability through Nafion 115 than methanol due to ethanol’s high molecular weight [70]. Lower ex-situ ethanol permeability was also observed in AEMs developed at University of Surrey [68]. Therefore, the lower limiting crossover current density for ethanol determined in this work was attributed to the lower permeability of larger ethanol
molecules in the AEM. However, more work is required to gain better understanding on
the crossover behavior of ethanol and methanol, and their use as a fuel in AMFC.

6.4 Concluding Remarks

In this work, MEAs were developed for direct ethanol AMFC, in which aqueous
hydroxide solution was not required during cell operation. It was found that the use of
wet-proof GDLs enhanced mass transport in the AMFC, reduced the cell internal
resistance, and improved the cell performance. It was also determined that best cell
performance was achieved with 6 to 8 wt.% ionomer content in the anode catalyst layer.
The maximum power densities achieved for direct ethanol AMFC using oxygen and air
as oxidant were 6.482 mW/cm² at 0.222 V and 3.380 mW/cm² at 0.130 V, respectively.
These results are the highest cell performance reported for direct ethanol AMFC.
However, the cell performance is still lower than that attained in PEM-based DEFCs.
The cell performance of the direct ethanol AMFC was found to be significantly improved
with the addition of potassium hydroxide. This shows the insufficient hydroxide
conductivity in the MEAs in the absence of potassium hydroxide. The addition of
potassium hydroxide may also increase reaction kinetics.

Methanol was also used as a fuel in the AMFC, and it was found that the
performance was substantially lower than that using ethanol as fuel. This is attributed to
severe poisoning of the cathode due to the ease of methanol crossover in the thin
membrane used in this study.
Table 10  Densities of catalyst, carbon and carbon-supported catalysts in g/cm$^3$.

<table>
<thead>
<tr>
<th></th>
<th>Pt</th>
<th>Ru</th>
<th>PtRu</th>
<th>$C_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>21.46</td>
<td>12.45</td>
<td>17.21</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.14</td>
</tr>
<tr>
<td>40 wt.% M on C</td>
<td>1.84</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80 wt.% M on C</td>
<td>4.71</td>
<td>-</td>
<td>4.51</td>
<td>-</td>
</tr>
</tbody>
</table>

Pt = platinum, Ru = ruthenium, and $C_p$ = porous carbon

Density of metal alloy or carbon-supported catalyst can be calculated as follows,

$$\frac{1}{\rho} = \frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}$$

where $\rho$ and $x$ are the density and mass fraction, respectively.
Table 11  Maximum power density and HFR of AMFC with different ionomer contents and operating with ethanol/oxygen and ethanol/air.

<table>
<thead>
<tr>
<th>Ionomer Content (wt.%)</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EtOH/O₂</td>
<td>EtOH/Air</td>
</tr>
<tr>
<td>6</td>
<td>6.482</td>
<td>3.218</td>
</tr>
<tr>
<td></td>
<td>(at 0.222 V)</td>
<td>(at 0.149 V)</td>
</tr>
<tr>
<td>8</td>
<td>6.248</td>
<td>3.380</td>
</tr>
<tr>
<td></td>
<td>(at 0.246 V)</td>
<td>(at 0.130 V)</td>
</tr>
<tr>
<td>10</td>
<td>5.640</td>
<td>3.175</td>
</tr>
<tr>
<td></td>
<td>(at 0.193 V)</td>
<td>(at 0.147 V)</td>
</tr>
</tbody>
</table>
Table 12 Maximum power density and HFR of AMFC using ethanol and methanol as fuel.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>High Frequency Resistance (Ω·cm²)</th>
<th>Open-Circuit Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>5.636 (at 0.193 V)</td>
<td>0.301</td>
<td>0.723</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.547 (at 0.057)</td>
<td>0.430</td>
<td>0.670</td>
</tr>
</tbody>
</table>
Figure 52  Effect of PTFE-treatment on GDL on cell performance. (Membrane A901, $T_{cell} = 50^\circ C$, $F_{E_{\text{OH}}} = 1 \text{ L/min}$, $F_{O_2} = 0.2 \text{ L/min}$, $RH_{O_2} = 100\%$, $p_{O_2} = 1 \text{ atm}$, absolute)
Figure 53  Effect of ionomer content on cell performance. (Membrane A901, T_{cell} = 50°C, \(F_{\text{EtOH}} = 1\ L/min\), \(F_{O2} = 0.2\ L/min\), \(RHO2 = 100\%\), \(pO2 = 1\ atm\), absolute)
Figure 54  Effect of ionomer content on cell performance. (Membrane A901, T_{cell} = 50^\circ C, F_{E_{10H}} = 1 \text{ L/min}, F_{air} = 0.2 \text{ L/min}, R_{H_{air}} = 100\%, p_{air} = 1 \text{ atm, absolute})
Figure 55  Effect of Addition of KOH on cell performance. (Membrane A901, T\textsubscript{cell} = 50°C, F\textsubscript{EtOH} = 1 L/min, F\textsubscript{O2} = 0.2 L/min, RH\textsubscript{O2} = 100%, p\textsubscript{O2} = 1 atm, absolute)
Figure 56  Effect of fuel type on cell performance. (Membrane A901, T\textsubscript{cell} = 50°C, F\textsubscript{Fuel} = 1 mL/min, F\textsubscript{O2} = 0.2 L/min, RH\textsubscript{O2} = 100%, p\textsubscript{O2} = 1 atm, absolute)
Figure 57  Ethanol and methanol crossover in AMFC. (Membrane A901, \( T_{\text{cell}} = 50^\circ\text{C} \), \( F_{\text{Fuel}} = 1 \text{ mL/min} \), \( F_{\text{N}_2} = 0.2 \text{ L/min} \), \( R_{\text{H}_2} = 100\% \), \( p_{\text{N}_2} = 1 \text{ atm, absolute} \))
7.1 Conclusions

In the first part of this project, the performance of AMFC using commercial non-platinum-based electrodes and AEM was evaluated. Using a fuel blend that consists of ethanol, potassium hydroxide, hydrazine and water, the AMFC attained maximum power densities of 16.8 mW/cm² and 20.6 mW/cm² at 25°C and 40°C, respectively. The overall performance of the fuel cell was by a high HFR value of 6.7 Ω·cm². It was noted that the performance of the AMFC was strongly dependent on the addition of hydrazine. Without the addition of hydrazine, the maximum power density was significantly reduced. The performance of the AMFC was found to be further reduced upon the elimination of aqueous potassium hydroxide.

The second part of this project was focused on the development of a high performance MEA for an all-solid-state AMFC, in which liquid electrolyte is not required during operation of the fuel cell. In the developmental study, platinum-base catalysts were used and hydrogen was used as fuel to facilitate the diagnostic of the fuel cells. Thinner AEMs were used in the MEAs due to the lower ionic conductivity. Direct coating of catalysts on AEM was found to be the best fabrication technique for MEAs. An ionomer content of 20 wt.% was determined to generate the largest ECA at 13.9 m²/g. The AMFC was characterized by a low HFR value of 0.304 Ω·cm² and the maximum
power densities attained with the use of ambient air and pure oxygen were 102 mW/cm² and 204 mW/cm², respectively.

The performance of AMFCs was found to be influenced by exposure to carbon dioxide during material storage or during supply of air during operation. Absorption of carbon dioxide in the AEM and ionomer resulted in the formation of carbonate and bicarbonate anions. As a consequence, the conductivity and alkalinity dropped and the cell performance was reduced. Pre-treatment of CCM with potassium hydroxide was found to be a critical step in restoring the hydroxide conductivity in the MEA. In addition, the exposure to carbon dioxide can be minimized by conditioning the AMFCs using pure oxygen and operating the fuel cell using pure air instead of ambient air. By adopting these new understandings in the testing procedure, the performance of the AMFC was further improved. The AMFC was demonstrated with maximum power densities of 365 mW/cm² with hydrogen/oxygen and 213 mW/cm² with hydrogen/pure air. These maximum power density values are the highest reported in the literature to date.

Although reasonable performance has been demonstrated in the AMFC, its stability during cell operation remains a major concern. The AMFC stability was found to be dependent on the amount of ionomer in the catalyst layers with higher ionomer content improving the stability of the fuel cell. The performance degradation was significantly accelerated when the fuel cell was operated at higher current density. The poor stability was attributed to degradation of ionomer in the catalyst layer, especially at the catalyst/ionomer interfaces. The degradation of ionomer was also reflected in the loss of ECA in MEA after stability testing.
In the preliminary investigation on the water transport behavior in the AMFCs, water was found to be transported from the anode to the cathode side, which may be helpful to membrane hydration and the cathode ORR. However, the transported water may also lead to flooding at the cathode.

The use of liquid fuel was examined again in the final part of this project. New MEAs were developed for direct ethanol AMFC, in which aqueous hydroxide solution was not used during cell operation. Wet-proof GDLs was found to enhance mass transport in the AMFC and improve the performance of the fuel cell. It was determined that best cell performance was achieved with 6 to 8 wt.% ionomer content in the anode catalyst layer. It was shown that maximum power densities achieved in the direct ethanol AMFC using oxygen and air as oxidant are 6.482 mW/cm² and 3.380 mW/cm², respectively. These results are the highest peak power reported for direct ethanol AMFCs in the literatures. However, the cell performance is still lower than that attained in PEM-based DEFCs. Significant work is still necessary in advancing the AMFC technology for direct alcohol fuel cell applications.

7.2 Future Work

Reasonable performance has been demonstrated in hydrogen AMFC and direct ethanol AMFC. However, the performance of the fuel cells are still substantially below that attained in more developed fuel cell systems, such as PEMFC and DMFC. Therefore, considerable work is still required in developing the AMFC technology. Some of the suggestions for future work are discussed here.
**MEA Optimization** - One of significant insufficiencies in the developed MEAs is the low ECA measured in the catalyst layer. Detailed investigation on the structure of the catalyst layer would provide significant insight on the ionomer distribution and coverage in the catalyst layer, and facilitate the design and optimization of future MEAs. Ionomer solution is a key component in the fabrication of MEAs. Apart from sufficient hydroxide conductivity, new solubilized ionomer with “hydrophilic and hydrophobic cluster” structure similar to that of Nafion would be beneficial in AMFC applications. In lieu of Nafion-like alkaline ionomer, organic surfactant can be added in the formulation of the catalyst ink to alter the interaction behavior of the ionomer and catalyst powder. However, the effect of the surfactant should be fully examined to realize an optimized catalyst structure for AMFC.

**Stability of AMFC** – The stability of AMFC is still a major challenge which requires considerable research effort to improve the commercial value of AMFC. The performance reduction has been attributed to the degradation of ionomer and possible AEM in the MEA. In-situ examination on the catalyst layer would be very useful in determining the degradation and its dependence on composition and structure of the catalyst layer. Transparent cells, often used in imaging of water behavior in PEMFC, can be adopted to provide a window for imaging material and structural changes.

**Water Transport in AMFC** – The management of water in AMFC would require a new strategy due to the fact that water is a reactant for oxygen reduction reaction at the cathode and consumed in the hydrogen oxidation reaction at the anode. The transport of water through the membrane would also be via electro-osmotic drag from the cathode to the anode. Therefore, the cathode in AMFC is prone to drying out. However, the
preliminary finding in the current work showed that water was transported from the anode to the cathode at low current density. Further investigation should be carried out to understand the water transport behavior and its dependence on parameters such as operating temperature, level of gas humidification and operating current density etc.

*Direct Alcohol AMFC* – The performance of direct alcohol AMFC is substantially lower than that achieved in PEM-based fuel cells. The catalysts used in this study are optimized for methanol oxidation and oxygen reduction in acidic condition. Considerable evaluation work needs to be performed to determine the best catalyst system for AMFC application. In addition, the hydroxide conductivity was found to be insufficient. Therefore, development of new ionomer, especially one with a high tolerant to carbon dioxide, is essential.
References


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Educational Qualifications

- Degree of Doctor of Philosophy, May 2009
  - Materials Science and Engineering
  - The Pennsylvania State University, USA

- Degree of Master of Engineering, March 2002
  - Mechanical and Production Engineering
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- Degree of Bachelor of Engineering (First Class Honors), July 1999
  - Mechanical and Production Engineering
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Research Experience and Interests

- Sep 2003 to date
  - Research Assistant
  - The Pennsylvania State University (Electrochemical Engines Center)
  - Research work includes micro fuel cells, direct methanol fuel cells, alkaline membrane fuel cells

- Jul 2001 to Aug 2003
  - Research Engineer
  - Singapore Institute of Manufacturing Technology (formerly GINTIC)
  - Research work includes MEMS packaging, wafer processes

- Jul 1999 to July 2001
  - Research Scholar
  - Nanyang Technological University, Singapore
  - Research work includes ageing and creep of magnesium alloys at elevated temperatures

Conference Presentations and Publications

