APPLICATIONS OF POLYAMIDOAMINE DENDRIMERS IN POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

by

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A DISSERTATION

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ABSTRACT

Dendrimers are highly branched macromolecules with well-ordered three-dimensional architectures. Polyamidoamine (PAMAM), the most common class of dendrimers, have been widely studied due primarily to the following three features: 1) the interior amine and amide groups that can interact with ionic metal precursors through ligand exchange reactions; 2) the presence of an interior void space in the higher generation dendrimers; and 3) the exterior primary amine groups that permit further functionalization. These unique structural features have inspired many potential applications. This dissertation describes two applications of PAMAM dendrimers in polymer electrolyte membrane fuel cells (PEMFCs).

First, in an effort to improve the utility of Pt in PEMFCs, PAMAM G4 was used as both a template and a stabilizer to synthesize dendrimer encapsulated Pt nanoparticles (Pt DENs) by photoreduction. These nanoparticles are highly monodisperse, exhibit high specific activity for the oxygen reduction reaction, and are inert to methanol oxidation, showing great potential for application in PEMFCs. Then, a simplified membrane electrode assembly (MEA) has been fabricated by the electrostatic self-assembly between Nafion® and Pt DENs and characterized. Two methods were proposed to increase Pt loading: layer-by-layer self-assembly and immobilization of Pt DENs and carbon powder on carbon fibers. Approximately 80 layers were proposed to reach the required loading using a dipping machine. Immobilization of Pt DENs and
carbon powder simultaneously on carbon fibers can easily be achieved by electrochemical coupling, which is promising for replacing the conventional method of electrode fabrication.

Secondly, in order to reduce the methanol crossover in direct methanol fuel cells (DMFCs), PAMAM G0 doped Nafion® membranes were prepared. Direct TEM imaging of the Naifon® embedded with nanoparticles demonstrates that PAMAM G0 can penetrate into the bulk of Nafion® through cluster channels to re-organize the distribution of sulfonate clusters by interacting with the sulfonic acid groups in different clusters. The presence of PAMAM G0 in the Naifon® membrane causes reduction of both methanol permeability and proton conductivity, but a very beneficial trade off can be reached when a doping concentration of $10^{-4}$ M PAMAM G0 is used. The fuel cell performance is much improved when Naifon® was treated with $10^{-4}$ M PAMAM G0.
# LIST OF ABBREVIATIONS OR SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection Fourier transform infrared</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
</tr>
<tr>
<td>DENs</td>
<td>Dendrimer encapsulated nanoparticles</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EW</td>
<td>Equivalent weight</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GCE</td>
<td>Glassy carbon electrode</td>
</tr>
<tr>
<td>H$_2$-PEMFC</td>
<td>Hydrogen-polymer electrolyte membrane fuel cell</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand-to-metal charge transfer</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
</tbody>
</table>
ORR Oxygen reduction reaction
PAFC Phosphoric acid fuel cell
PAMAM Polyamidoamine
PEM Polymer electrolyte membrane
PFAE Perfluoroalkylether
PTFE Polytetrafluoroethylene
RE Reference electrode
SAXS Small-angle X-ray scattering
SCE Saturated calomel electrode
SEM Scanning electron microscopy
SOFC Solid oxide fuel cell
TEM Transmission electron microscopy
WE Working electrode
XPS X-ray photoelectron spectroscopy

A Area of the membrane
P Methanol permeability
R Resistance of the membrane
S Cross-sectional area of the membrane
Z Impedance
f Cyclic frequency
l Thickness of the membrane
β Semi-angle of collection of the magnifying lens
δ Resolution
\( \theta \)  
Phase difference between the voltage and current

\( \lambda \)  
Wavelength

\( \omega \)  
Angular frequency

\( \phi \)  
Work function
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CHAPTER 1
INTRODUCTION

1.1 Fuel Cells

Fuel cells are environmentally friendly electrochemical devices that convert the chemical energy of fuels into electrical energy directly and are often regarded as one of the most promising energy technologies of the future.¹

The fuel cell was first invented by Sir William Grove in 1839. During the first hundred years, although many electrochemists devoted lots of efforts to the study of the fuel cell, its development was slow due to the high cost, limited materials, and low operational efficiencies. The first successful application of a fuel cell was conducted by NASA for the Gemini and Apollo space programs in the 1960s.² This opened a new era of fuel cell development by demonstrating their power and advantages. Nowadays, all of the major automotive manufacturers are working to commercialize their fuel cell powered cars.

In a typical fuel cell, as shown in Figure 1.1, the fuel is fed continually to the anode and the oxidant gas is fed continually to the cathode. Electrochemical reactions then occur at the electrodes to produce an electric current through the load.

Although a fuel cell is similar to a battery in many ways, it differs in several respects. The battery is an energy storage device, and the maximum energy is determined by the amount of chemical reactants stored within it. Therefore, the lifetime of a battery is
Figure 1.1. Schematic drawing of a PEMFC system.
limited. In comparison, the fuel cell is only an energy conversion device. In principle, the lifetime of a fuel cell is unlimited as long as the reactants and products are continually supplied and removed, respectively. Compared to internal combustion engines, fuel cells have several advantages. Internal combustion engines convert the chemical energy of a fuel into thermal energy, and then convert thermal energy into mechanical energy. However, fuel cells directly convert chemical energy into electrical energy. Therefore, fuel cells have a higher efficiency than internal combustion engines. The power generation of fuel cells is accomplished without moving parts, so less maintenance is required. Lastly, fuel cells are clean. If a fuel cell uses hydrogen as the fuel, the products are only water, heat, and electricity.¹

1.1.1 Classification of Fuel Cells

Fuel cells are usually classified according to the choice of fuel and electrolyte, which determines the electrode reactions and the type of ions that transfer the current across the electrolyte. Fuel cells are classified as either a polymer electrolyte membrane fuel cell (PEMFC) [including H₂-PEMFC and direct methanol fuel cell (DMFC)], an alkaline fuel cell (AFC), a phosphoric acid fuel cell (PAFC), a molten carbonate fuel cell (MCFC), or a solid oxide fuel cell (SOFC). Table 1.1 briefly shows their characteristics, advantages and disadvantages.¹ H₂-PEMFC and DMFC will be discussed at length in this Chapter.

1.1.2 Hydrogen-Polymer Electrolyte Membrane Fuel Cells

Among all fuel cells, the hydrogen-polymer electrolyte membrane fuel cell (H₂-PEMFC) is considered to be one of the most promising energy conversion devices. The
Table 1.1. Classification of fuel cells.¹

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>DMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Ion exchange membrane</td>
<td>Ion exchange membrane</td>
<td>Immobilized alkaline salt</td>
<td>Immobilized liquid phosphoric</td>
<td>Immobilized liquid molten</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>50~80 °C</td>
<td>20~90 °C</td>
<td>50~200 °C</td>
<td>175~220 °C</td>
<td>600~350 °C</td>
<td>800~1000 °C</td>
</tr>
<tr>
<td>Charge carrier</td>
<td>H⁺</td>
<td>H⁺</td>
<td>CH⁻</td>
<td>H⁺</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Efficiency</td>
<td>40~50%</td>
<td>25~40%</td>
<td>50~70%</td>
<td>40~45%</td>
<td>50~60%</td>
<td>50~60%</td>
</tr>
<tr>
<td>Application</td>
<td>Portable, mobile</td>
<td>Portable mobile</td>
<td>Space</td>
<td>Electric utility</td>
<td>Electric utility</td>
<td>Electric utility</td>
</tr>
<tr>
<td>Advantages</td>
<td>High power density &amp; low temperature</td>
<td>No reforming, high power density &amp; low temperature</td>
<td>High efficiency</td>
<td>Tolerant to impure H₂, commercial</td>
<td>High efficiency, near commercial</td>
<td>High efficiency &amp; direct fossil fuel</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Intolerant to CO &amp; expensive</td>
<td>Low efficiency, methan crossover &amp; poisonous byproduct</td>
<td>Intolerant to CO₂, corrosion &amp; expensive</td>
<td>Low power density, corrosion &amp; sulfur poisoning</td>
<td>Electrolyte instability, corrosion &amp; sulfur poisoning</td>
<td>High temperature, thermal stress failure, coking &amp; sulfur poisoning</td>
</tr>
</tbody>
</table>
main component of a PEMFC is the membrane electrode assembly (MEA). The schematic drawing of an MEA is shown in Figure 1.2. An MEA is a “sandwich” consisting of two electrodes (two catalyst layers and two diffusion layers) and an electrolyte [a polymer electrolyte membrane (PEM)]. The PEM is “sandwiched” between the two catalyst layers. The catalyst layers are either coated or sputtered onto the gas diffusion layers. The main advantages of MEAs are the high mass transport rate, low weight, low resistance, and the fact that they can be easily scaled up to form fuel cell stacks to achieve the voltage required for the application.\(^3\)

![Figure 1.2. Schematic drawing of an MEA.](image-url)
1.1.2.1 H$_2$-PEMFC Electrodes

A H$_2$-PEMFC electrode is composed of a porous carbon paper/cloth and a catalyst layer. The main function of electrodes in fuel cells is to provide a surface for electrochemical reactions to take place.

In a typical H$_2$-PEMFC, as shown in Figure 1.1, the anode is fed continuously with hydrogen, and the cathode is fed with oxygen. Hydrogen is oxidized on the anode, and oxygen is reduced on the cathode, and electrons flow from anode to cathode through the load. The reactions in a H$_2$-PEMFC can be expressed by the following equations.

Anode: \[ H_2 \rightarrow 2H^+ + 2e^- \] \[ [1.1] \]

Cathode: \[ 2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O \] \[ [1.2] \]

Overall: \[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \] \[ [1.3] \]

Compared to the oxidation of hydrogen, the kinetics of the reduction of oxygen are much slower. The exchange current density for oxygen reduction is ca. $10^{-6}$ times lower than that for hydrogen oxidation on Pt catalysts.\(^4\) Also, oxygen reduction is a 4-electron, multi-step process, and it involves several pathways.\(^5\) Several models have been proposed to describe the oxygen reduction reaction mechanism.\(^6\)\(^-\)\(^8\) It is generally agreed that the first step of oxygen reduction on Pt catalysts is the adsorption of oxygen on the surface of the catalyst. Therefore, the kinetics of oxygen reduction are highly dependent on the structure and size of the catalyst.\(^9\)

The most common methods used for fabricating electrodes are painting, spraying or physical impregnation of a catalyst ink onto the carbon paper. The structure of the catalyst layer is crucial to the performance of an electrode. The catalyst layer is a
heterogeneous four-phase mixture, which is composed of the carbon support, the catalyst, the electrolyte, and gas filled pores. The catalyst layer must have good electronic and ionic conductivities. Electronic conductivity is provided by the carbon support, while the ionic conductivity is granted by recast Nafion®. Also, the catalyst layer must have hydrophobic channels to allow gas access to the catalyst. Optimization of the structure of electrodes has been the subject of intensive study and will be discussed in detail in Chapter 3.

1.1.2.2 H₂-PEMFC Electrolyte

The polymer electrolyte membrane (PEM) is a crucial part of the H₂-PEMFC. It works as both the electrolyte and the separator between hydrogen and oxygen. Although many kinds of polymer membranes, including non-fluorinated, partially fluorinated, and perfluorinated, have been developed, Nafion® discovered by DuPont in the 1960s is still the most often employed electrolyte.

Nafion® is generated by the copolymerization of a perfluorinated vinyl ether comonomer with tetrafluoroethylene. The chemical structure of Nafion® is shown in Figure 1.3. Nafion® has a polytetrafluoroethylene (PTFE) backbone and perfluoroalkylether (PFAE) side chains with terminating sulfonic acid groups (-SO₃H). The Teflon-like backbone provides Nafion® with excellent thermal and mechanical stability, while the sulfonic acid groups provide them with high proton conductivity when well hydrated. The mass of polymer per mole of sulfonic acid groups is referred to as equivalent weight (EW). Increasing EW improves mechanical properties, but decreases proton conductivity. 1100 EW Nafion® is typically used in H₂-PEMFCs because it has a reasonable balance of proton conductivity and mechanical stability.
The detailed configuration of Nafion® is still not clear. It is generally believed that there are two phases in the membrane: one is the hydrophobic phase composed of the PTFE backbone, and the other is the hydrophilic phase composed of the sulfonic acids and water. The first model for Nafion® is cluster-network model proposed by Gierke and Hsu.\textsuperscript{11-13} As shown in Figure 1.4, the sulfonate ion clusters with a $\sim 4$ nm diameter are organized as inverted micelles and held on a perfluorocarbon lattice. These micelles are connected by proposed channels that are $\sim 1$ nm in size. This model provides a conceptual basis for rationalizing the properties of Nafion® membranes, especially ion and water transport.\textsuperscript{10}
Figure 1.5 shows evolution of the membrane structure as a function of water content.\textsuperscript{14} In the dehydrated conditions, strong ionic interactions exist, as shown in panel a. Once hydrated, the hydrophilic cluster will expand, water becomes less bound, and inverted micelles form in the fluorocarbon matrix. With more water uptake, the hydrophilic clusters further enlarge and form interconnections with each other, as shown in panel d. The transport of molecules and ions are facilitated through this interconnected ionic network. It is evident from several investigations that the diffusion of ions and molecules is affected by ionic nanostructure.\textsuperscript{15,16}

The major drawback to Nafion\textsuperscript{®} as the ideal PEM in H\textsubscript{2}-PEMFCs is that the conductivity drops at temperatures higher than 80 °C due to the evaporation of water, which limits the operating temperature of H\textsubscript{2}-PEMFCs. Currently, the target operating temperature of H\textsubscript{2}-PEMFCs is 120-150 °C. The relatively high temperature will increase the fuel cell CO tolerance, and reduce the problems of the thermal management of the H\textsubscript{2}-PEMFC stack.

1.1.2.3 Advantages and Disadvantages

The H\textsubscript{2}-PEMFC gives high power density and high efficiency. Because the H\textsubscript{2}-PEMFC uses a non-corrosive solid polymer electrolyte, it results in excellent resistance to gas crossover and a simpler design that requires less maintenance. In addition, since the only liquid in this fuel cell is water, corrosion problems are minimal. However, water management is important for efficient performance, because dehydration of the membrane decreases proton conductivity and an excess of water can lead to flooding of the electrodes. A second issue about H\textsubscript{2}-PEMFCs is CO poisoning. When fuels that usually contain CO are used, the CO will bind to the surface of catalyst and deactivate
Figure 1.5. Evolution of the membrane structure as a function of water content (Adapted from reference 14).
the catalyst. For low temperature H\textsubscript{2}-PEMFC, the tolerance for CO is only 10-20 ppm. However, if H\textsubscript{2}-PEMFC can operate at high temperature, the tolerance can reach thousands of ppm. Therefore, a higher operating temperature is the target for the development of H\textsubscript{2}-PEMFC. A third disadvantage of a H\textsubscript{2}-PEMFC is its high cost, which is mainly due to the platinum-based catalyst and the fluorinated polymer electrolyte membrane.\textsuperscript{1}

1.1.3 Direct Methanol Fuel Cells

The direct methanol fuel cell (DMFC) has attracted much interest in the field of portable electronic devices. It has the potential to offer 10 times higher power density than a lithium-ion rechargeable battery.\textsuperscript{17} The principle of a DMFC is very similar to that of a H\textsubscript{2}-PEMFC, where both use a PEM as the electrolyte. However, in a DMFC, methanol, instead of hydrogen, is used as the fuel. Compared with a hydrogen fuel cell, a DMFC has many advantages, such as, ease of storage and transport of the fuel, a simpler system, and a higher energy density by volume. Recently, a number of companies, such as Toshiba, Hitachi and Sanyo, have developed prototype laptops and cellular phones that are powered by a DMFC.

1.1.3.1 DMFC Electrodes

In a DMFC, aqueous methanol (generally ca. 1-2 M) is pumped into the anode where the methanol is oxidized. The reaction occurring on the anode is shown as below.

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6e^- \quad [1.4]
\]
The protons as the current carrying ions pass through the polymer electrolyte to reach the cathode, and the electrons are transported via external circuit to arrive on the cathode. The reaction occurring on the cathode is

\[ \frac{3}{2} O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \]  

[1.5]

The overall direct methanol fuel cell reaction is

\[ CH_3OH + \frac{3}{2} O_2 \rightarrow 2H_2O + CO_2 \]  

[1.6]

Although lots of progress has been made in the development of DMFC, its performance is still limited by the slow oxidation kinetics of methanol. The oxidation of methanol consists of a series of successive reactions creating formaldehyde and formic acid that slow down the reaction rates and decrease the cell voltage.\textsuperscript{18} At present, the investigation of new anode catalysts to improve oxidation rates is a very active field of research.

1.1.3.2 DMFC Electrolyte

Methanol crossover through the PEM contributes to the reduction of overall cell efficiency and lifetime. Most DMFCs use Nafion\textsuperscript{®} as the electrolyte. However, Nafion\textsuperscript{®} is permeable to methanol, resulting in high methanol crossover from the anode to the cathode. It has been reported that up to 40% of the methanol can be wasted in DMFCs.\textsuperscript{19} Besides the methanol loss, the reaction of methanol at the cathode results in a loss of cathode voltage. Usually, in order to reduce methanol crossover, low methanol concentration (1-2 M) is used in DMFC, which limits the overall cell potential. Current DMFCs have an open circuit voltage of ~0.7 V, which is only a little more than half of the reversible “no-loss” cell voltage of ~1.2 V.\textsuperscript{20} This issue will be discussed in detail in the Chapter 4.
1.2 PAMAM Dendrimer

Dendrimers are highly branched macromolecules with well-ordered three-dimensional architectures. They are widely recognized as the fourth major class of polymers after linear polymers, cross-linked polymers and branched polymers. Each dendrimer molecule has three common structural features: a central molecular core, repetitive branches, and terminal groups. The dendrimer structure is characterized by layers between each focal point termed generations (G). PAMAM, the most common class of dendrimers, was first invented by Tomalia in the early 1980s. Some physical properties of PAMAM dendrimers with generations from 0 to 5 are listed in Table 1.2. With each new layer that is synthesized, the molecular weight of the dendrimer increases exponentially, the number of primary amine surface groups exactly double and the diameter increases by roughly 1 nm. Lower generation dendrimers have a planar or elliptical shape, while at the higher generations, the densely packed branches cause the polymer to form a spherical structure. Starting from G4, the interior of the dendrimer develops void spaces that can be used to encapsulate molecules.

PAMAM dendrimers can be prepared by two different routes: the divergent approach and the convergent approach. In the divergent method, the synthesis starts from an ethylenediamine core and proceeds outwards by consecutive stepwise activation and condensation. In the convergent method the synthesis starts at the periphery of the final macromolecule and proceeds inwards. The dendrimers prepared from convergent method are more monodisperse because the impurities produced in this process can be easily removed by chromatography. However, due to
Table 1.2. Physical properties of PAMAM dendrimers\textsuperscript{23}.

<table>
<thead>
<tr>
<th>Generation</th>
<th>Number of Surface Groups</th>
<th>Number of Tertiary Amine</th>
<th>Diameter (nm)</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>2</td>
<td>1.5</td>
<td>517</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>6</td>
<td>2.2</td>
<td>1,430</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>14</td>
<td>2.9</td>
<td>3,256</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>30</td>
<td>3.6</td>
<td>6,909</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>62</td>
<td>4.5</td>
<td>14,215</td>
</tr>
<tr>
<td>5</td>
<td>128</td>
<td>126</td>
<td>5.4</td>
<td>28,826</td>
</tr>
<tr>
<td>6</td>
<td>256</td>
<td>254</td>
<td>6.7</td>
<td>58,048</td>
</tr>
</tbody>
</table>
the low reaction yield between high generation dendrons and the core, high generation (> G8) dendrimers cannot be prepared by the convergent method. The commercially available PAMAM dendrimers are prepared by the divergent approach. Figure 1.6 shows the synthesis of amine-terminated PAMAM dendrimers. The preparation of PAMAM dendrimers is composed of a reiterative sequence of two basic reactions: the Michael addition reaction of amino groups to the double bond of methyl acrylate, and the amidation of the resulting methyl ester with ethylenediamine.

PAMAM dendrimers have been widely studied due mainly to three unique features: 1) the interior amine and amide groups can interact with ionic metal precursors through ligand exchange reactions, which offers the possibility to prepare dendimer encapsulated nanoparticles; 2) the exterior of PAMAM G4 dendrimer is dense while its interior is relatively hollow, and the space between the terminal groups acts as a gate to only allow small molecules in; which is ideal for application as templating or encapsulating molecule; and 3) the exterior primary amine groups permit further functionalization, which can be utilized for surface modification.

1.3 Applications of PAMAM Dendrimers in Fuel Cells

The unique structure features of dendrimers have inspired many potential applications. The following section provides some successful applications of PAMAM dendrimers that are related to the research projects discussed in this dissertation.

1.3.1 PAMAM Dendrimers as Hosts for Synthesizing Nanoparticles

Supported catalysts are favored in industrial processes due to high dispersion of active components and the stability to keep these active components from
Figure 1.6. Synthesis and structure of PAMAM dendrimers.
agglomeration. One promising method of preparing supported catalysts on the nanoscale is using dendrimers as templates and stabilizers. It has been demonstrated by several groups that PAMAM dendrimers can complex metal ions to make metallic dendrimer encapsulated nanoparticles (DENs). The approach takes advantage of the fact that transition metal ions can coordinate with the interior amine groups of the dendrimer. The preparation process usually consists of two steps. First, a PAMAM solution and a metal ion solution are mixed at a desired stoichiometric ratio. This results in the complexation of the metal ions with interior functional groups of PAMAM. Second, the metal ion/PAMAM composites are reduced using excess NaBH₄ to yield PAMAM encapsulated metal nanoparticles.

In our study, the approach involves the use of amine-terminated PAMAM as both a template and a stabilizer to synthesize Pt nanoparticles by photoreduction. This will be discussed at length in Chapter 3.

### 1.3.2 PAMAM Dendrimers as Cross linker

PAMAM dendrimers have received lots of attention because of the high density of terminal amine group that provides a large number of reactive sites for many potential applications. For example, Crooks et al. demonstrated that PAMAM dendrimers could be attached to an activated mercaptoundecanoic acid to form self-assembled monolayer by covalent amide linkages. These surface-confined dendrimer monolayers were used as chemical sensors and catalytic interfaces.

In our study, PAMAM dendrimers are considered as multivalent counterions and are incorporated into the Nafion® membrane via a proton-exchange mechanism, where the basic amino groups accept protons from the sulfonic acid groups to form ammonium-
sulfonate pairs. Chapter 3 of this dissertation includes the procedure of attaching PAMAM G4 encapsulated Pt nanoparticles to Nafion® surface to form self-assembled MEA. Self-assembled monolayers prepared from PAMAM G4 are expected to show improved stability due to a large number of potential attachment points per molecule. In Chapter 4, PAMAM G0 was employed as the crosslinker to modify the commercial Nafion® membranes to reduce the methanol crossover for DMFC applications.

1.4 Outline of this Dissertation

In Chapter 1, the first part introduces the basic principles and different types of fuel cells. Details about H₂-PEMFCs and DMFCs are presented. In the second part of the introduction, the properties of PAMAM dendrimer are discussed.

In Chapter 2, the main analytical techniques used in this dissertation will be described, including transmission electron microscopy, scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, alternating current electrochemical impedance spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy, cyclic voltammetry, chloridometer, and gas chromatography.

In Chapter 3, the amine-terminated PAMAM G4 is proposed for use as both a template and a stabilizer to synthesize Pt nanoparticles by photoreduction. The details about synthesis and characterization of these particles will be presented. The specific activity of the synthesized particles for both the oxygen reduction and methanol oxidation reactions will be compared to the commercial Pt nanoparticles. Further, a novel method is introduced to fabricate a simplified MEA using the self-assembly of Pt
DENs on Nafion® to by electrostatic association. Finally, two methods aimed at increasing Pt loading are proposed and discussed in detail.

In Chapter 4, PAMAM G0 is introduced into the Nafion® membrane to enhance DMFC performance. The surface functional groups of the un-doped and doped membranes were determined using X-ray photoelectron spectroscopy. A change in the pore size after doping is also examined using TEM. Transport properties including proton conductivity and methanol permeability of doped Nafion® membranes are also studied. The effect of concentration of PAMAM G0 on the DMFC performance will be discussed in detail.

Chapter 5 summarizes and concludes this dissertation and presents issues about future directions in fuel cell research.
1.5 References


CHAPTER 2
THEORY OF SELECTED ANALYTICAL TECHNIQUES

This chapter covers the main analytical techniques used in Chapter 3 and Chapter 4, including transmission electron microscopy, scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, alternating current electrochemical impedance spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy, cyclic voltammetry, chloridometer, and gas chromatography.

2.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an advanced microscopic technique that provides high spatial resolution. Figure 2.1 shows a schematic diagram of a TEM. A high-energy electron beam is emitted from the electron gun, which then passes through the electromagnetic condenser lens to produce a small, thin, coherent beam. The beam interacts with the specimen mostly by diffraction, although the attenuation of the transmitted beam also depends on the density and thickness of the specimen. The transmitted electrons are focused and magnified by the electron optics to form an image on a fluorescent screen.

Typically, a TEM operating at 200 KV generates an electron beam with wavelength $\lambda = 0.03$ Å. According to the Raleigh criterion, resolution is directly proportional to
Figure 2.1. Schematic diagram of the transmission electron microscope.
wavelength

\[ \delta = 0.61\lambda/\beta \]  

[2.1]

where \( \delta \) is the resolution, \( \lambda \) is the wavelength and \( \beta \) is the semi-angle of collection of the magnifying lens. The smaller the wavelength, the better the resolution is. Hence the resolution obtained in a TEM can be on the order of few angstroms.\(^1\)

In this dissertation, the TEM images of Pt DENs were obtained using a FEI TECNAI F20 TEM, and the TEM images of Ag nanoparticles in Nafion\(^\text{®} \) membrane were obtained on a Hitachi 8000 TEM.

### 2.2 Scanning Electron Microscopy

Scanning electron microscope is a type of electron microscope that images the surface of a sample by scanning it with a beam of high-energy electrons. The electrons interact with atoms of the sample, producing signals that contain information about the surface topography and compositional properties of the sample. In a typical SEM, as shown in Figure 2.2, the electron beam emitted from the electron gun is focused by two condenser lenses to a spot. The beam passes through pairs of scanning coils that deflect the beam in the x and y directions. The interaction of the electron beam and the specimen results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of X-rays. Each of these signals is detected by a specific detector.\(^2\)

In this dissertation, the SEM analysis of carbon paper modified with Pt DENs and carbon powder was conducted on a JEOL 7000 operating at 20 KV.
Figure 2.2. Schematic diagram of the scanning electron microscope.
2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscopy with very high resolution. Unlike electron microscopes, AFM images the surface by “feeling” the atoms on the surface using a mechanical probe. Figure 2.3 shows the schematic drawing of an AFM system, which is composed of a tip attached to a cantilever, piezoelectric scanner, laser detector, and computer controller. The AFM can be operated in three different modes: contact, tapping, and non-contact mode. The tapping mode is the only mode used and described here. In the tapping mode, the cantilever is driven to oscillate up and down at or near its resonant frequency by a small piezoelectric crystal, and the oscillation amplitude remains constant by a feedback loop. When the tip passes through a bump or a depression on the surface, the amplitude will change from its previous amplitude of oscillation. A detector measures the amplitude of oscillation of the tip, and then the feedback loop adjusts the tip-sample separation to maintain constant amplitude on the sample. Therefore, a topographical image can be produced.3

In this dissertation, the AFM used to image the self-assembled MEAs was a Digital Instruments Dimension 3000. The silicon tips used have a radius of curvature less than 10 nm.

2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique based on the photoelectric effect. Figure 2.4 shows a schematic of the principle of XPS. When an X-ray beam strikes the surface of a sample, the energy of the photon is adsorbed by
Figure 2.3. Schematic diagram of the atomic force microscope.
a core electron of an atom. If the photon energy is large enough, the atoms in the sample surface will be ionized, which leads to the emission of the photoelectrons. The kinetic energy of these photoelectrons is measured by an analyzer. The binding energy (BE) is given by the Einstein relationship:

\[ BE = h \nu - KE - \phi \]  

Where \( h \nu \) is the X-ray photo energy, \( KE \) is the kinetic energy of photoelectron and \( \phi \) is the work function. The core electrons of an element have unique binding energies, and thus almost all elements can be identified by measuring the binding energies of its core electrons. Furthermore, the binding energy of a core electron is very sensitive to the chemical environment of element. If an atom is in a higher positive oxidation state, it will show a higher binding energy due to the extra coulomb interaction between the photoelectron and the ion core. Similarly, an atom of a lower negative oxidation state shows a lower binding energy. Therefore, XPS can be applied to study the chemical status of an element on the surface.

In this dissertation, X-ray photoelectron spectra of PAMAM G0 modified Nafion\textsuperscript{®} and self-assembled MEA were obtained with a Kratos Analytical Axis 165 Scanning Auger/X-ray Photoelectron Spectrometer.

### 2.5 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is based on the total reflection of electromagnetic radiation in the interface between two media having different refractive indices. Figure 2.5 shows a schematic illustration of the ATR principle. The sample is pressed into intimate contact with the surface of the
Figure 2.4. Schematic of principle of X-ray photoelectron spectroscopy.
crystal. An IR beam gets propagated through the crystal and produces an “evanescent” wave that extends beyond the surface of the crystal into the sample. This evanescent wave penetrates only a few microns into the sample. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the other end of the crystal and is passed to the detector. The system then generates an infrared spectrum.

In this dissertation, ATR-FTIR spectroscopy (JASCO FTIR-4100) was used to study the chemical structures of the self-assembled MEA.

2.6 Alternating Current Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an experimental method of characterizing electrochemical systems. This technique has been widely employed in fuel cell testing, biomolecular interactions, and microstructural characterization.\(^4\)

In AC impedance spectroscopy, a small sinusoidal current perturbation is applied to the cell over a wide frequency range.

\[ I(t) = I_m \sin(\omega t) \]  \hspace{1cm} [2.3]

The resulting current that is out-of-phase with the voltage is measured.

\[ V(t) = V_m \sin(\omega t + \theta) \]  \hspace{1cm} [2.4]

where, \(I_m\) and \(V_m\) are the amplitudes of the perturbation and the response signals. \(\theta\) is the phase difference between the voltage and current. \(\omega\) is the angular frequency.
Figure 2.5. Schematic illustration of the attenuated total reflection Fourier transform infrared principle.
where $f$ is the cyclic frequency. The impedance is represented by $Z$ and its magnitude is given by

$$|Z| = \frac{V_m}{I_m}$$

The proton conductivity measurements of PAMAM G0 modified Nafion® were carried out using a CH Instruments, Inc. Electrochemical Workstation (Model CHI 660A).

### 2.7 Cyclic Voltammetry

Cyclic voltammetry is one of the most frequently employed electrochemical methods for the study of electroactive species. Typically, a three-electrode system (Figure 2.6) is used to obtain stable cyclic voltammograms (CVs). The working electrode, usually made of platinum, gold, or glassy carbon, is where the electrochemical reaction takes place. The counter electrode, usually made of platinum, is used to make a connection to the electrolyte so that a current can be applied to the working electrode. The reference electrode, such as, saturated calomel electrode (SCE) or silver/silver chloride electrode (Ag/AgCl), has a fixed electrode potential, so the potential of the working electrode can be controlled versus the reference electrode.

In a typical cyclic voltammetry experiment, an excitation signal, which is the potential applied across the working electrode and the reference electrode, is a linear scan with a triangular waveform, as shown in Figure 2.7. A CV is obtained by measuring the current at the working electrode during the potential scan. The voltammogram is a display of current (y-axis) versus potential (x-axis).
Figure 2.6. Schematic of three-electrode electrochemical cell.

Figure 2.7. Cyclic voltammetry potential waveform.
In this dissertation, all CVs were obtained using a CH Instruments, Inc. Electrochemical Workstation (Model CHI 660A). The potential is graphed with more positive potentials to the left of the x-axis, and more negative potentials to the right of the x-axis. The cathodic current is plotted up the y-axis, and anodic current is plotted down the y-axis.

2.8 Chloridometer

The chloridometer is a very simple instrument that one can use to measure the concentration of chloride ions in an unknown sample. This instrument is based on the reaction of silver cations and chloride anions to form silver chloride precipitate. The reaction is performed at a constant rate by passing a direct current through a pair of silver electrodes that are immersed in an acidic solution. When the reaction reaches equilibrium, the current flowing between the electrodes increases and is detected by a sensing element. At this point, the instrument stops the counter. Therefore, the number of chloride ions in the sample is directly proportional to the total titration time.

The digital chloridometer used for this dissertation was purchased from Haake Buchler Instruments Inc.

2.9 Gas Chromatography

Gas chromatography (GC) is a method that can be used to separate and quantify volatile organic compounds. It is a very adaptable technique and has been used in many areas such as chemical manufacturing, food science, environmental, and pharmaceutical industries.
A GC system is composed of a mobile phase, an injection port, a column and a detector. In principle, a very small amount of sample is injected into the instrument through a rubber septum and is volatilized in a heated injector chamber. Then, the volatilized sample is swept by a stream of inert carrier gas such as helium (He), hydrogen (H\textsubscript{2}), or nitrogen (N\textsubscript{2}) through a GC column. As the sample travels through the column, the components go back and forth at different rates between the stationary and mobile phases, and thus are separated into pure components. After the components exit the GC column, they pass through a GC detector, e.g. a flame ionization detector (FID).

In this dissertation, the GC used to measure methanol permeability of PAMAM G0 modified Nafion\textsuperscript{®} is Agilent 6890 and FID detector.
2.10 References


CHAPTER 3
DENDRIMER ENCAPSULATED PLATINUM NANOPARTICLES: PREPARATION, CHARACTERIZATION, AND APPLICATIONS IN POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

3.1 Introduction

Among the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) is regarded as one of the most promising energy conversion devices. However, for this technology to be commercially competitive, not only its performance needs to be improved, but also its cost must be comparable to current energy conversion devices.\(^1\) It is generally accepted that improving the utility of noble metal catalysts (typically Pt) and lowering their loading are vital to the success of PEMFC technology. The most common methods used for fabricating electrodes are painting, spraying or physical impregnation of a catalyst ink onto the carbon paper.\(^2\) Usually, the catalyst ink is prepared by dispersing a carbon black supported Pt particles in isopropanol and mixed with Nafion\(^\circledR\) solution by sonication. However, due to the agglomeration of Pt/C powders, the Pt particles are not always in direct contact with the electrolyte (Nafion\(^\circledR\)), even though the Pt/C powders and the electrolyte are mixed thoroughly. It has been reported that there are two pore size distributions in the catalyst layer: primary pores with size from 0.02 to 0.04 \(\mu\text{m}\) and secondary pores with size from 0.04 to 0.1 \(\mu\text{m}\).\(^3,4\) The electrolyte cannot penetrate the primary pores and only forms a
network within secondary pores of the electrode, as shown in Figure 3.1. Those electrocatalyst sites (in dash circle), which are in the primary pores and isolated from the electrolyte, will not be utilized because protons cannot be transported to these electrocatalyst sites to perform fuel cell reactions. Another drawback is that the nano scale catalyst has a high surface area and tends to aggregate to reduce its surface energy. Therefore, in order to reach required performance, these conventional catalyst layers generally featured high platinum loadings. Much effort has been put on the development of electrodes with high utility of noble metal catalysts. Such as, Xiong et al.\textsuperscript{5} directly deposited the catalyst layer onto the Nafion\textsuperscript{®} membrane and heat-treated the MEA at a low temperature (< 100 °C). The performance of the MEA showed higher Pt utilization efficiency and power density. Wei et al.\textsuperscript{6} directly deposited Pt on the surface of Nafion\textsuperscript{®}-bonded carbon electrode using electrodeposition method and claimed that the electrode performance was much better compared to a conventional electrode. O’Hayre et al.\textsuperscript{7} and Huang et al.\textsuperscript{8} and demonstrated that plasma sputter deposition technique has a high potential for MEA fabrication to reduce cell costs by achieving ultra-low levels of Pt catalyst loading.

Dendrimer templating was demonstrated as one of the methods for preparing very well defined, electrocatalytically active nanoparticles for the following two reasons: 1) dendrimers are uniform in structure and composition, and therefore they yield monodispersed nanoparticles; 2) dendrimers are highly permeable and do not passivate the surface of the encapsulated nanoparticles.\textsuperscript{9,10} Crooks and other groups have reported the preparation of PAMAM encapsulated Pt nanoparticles using chemical reduction.\textsuperscript{11-16} Their process consists of two steps. First, a PAMAM solution and a
Figure 3.1. The interface in an electrode consisting of the Nafion®, the carbon support, the catalyst particles, and the gas filled pores.
metal ion solution are mixed at a desired stoichiometric ratio. This results in the complexation of the metal ions with functional groups of PAMAM. Second, the metal ion/PAMAM composites are reduced using excess NaBH₄ to yield PAMAM encapsulated Pt nanoparticles. The main disadvantage of chemical reduction is that using NaBH₄ as the reducing agent can easily “poison” the Nafion® membrane during the self assembly process.¹⁷ Imae et al. synthesized crown-shaped particles with a size of 100 to 130 nm by UV irradiation in the presence of PAMAM-NH₂.¹⁸

The approach herein involves the use of amine-terminated PAMAM as both a template and a stabilizer to synthesize Pt nanoparticles by photoreduction and then self assembly of Pt DENs on Nafion® to form a simplified MEA by electrostatic association, as shown in Figure 3.2. This approach can produce electrocatalysts with decreased amounts of Pt and good dispersion, and the electrocatalysts are stabilized by encapsulation within the dendrimers, and therefore they do not agglomerate, which can maximize the active area and improve catalyst efficiency. The MEA can be easily fabricated and will have less proton transport loss due to a higher density of functional groups of PAMAM-NH₂ directly attached on the Nafion® surface.

3.2 Experimental

3.2.1 Materials

Amine-terminated fourth-generation polyamidoamine (PAMAM-NH₂ G4) was obtained as a 10% methanol solution (Aldrich-Sigma). Prior to use, the methanol was removed under vacuum at room temperature. The compounds H₂PtCl₆ and LiClO₄ (Aldrich-Sigma) were used without further purification. Deionized water (18 MΩ·cm
Figure 3.2. Schematic illustration of synthesis of Pt DENs and formation of simplified MEA.
Milli-Q) was used to prepare aqueous samples. The cellulose dialysis sacks (Aldrich-Sigma) have a molecular weight cut off of 12,000. Commercial Pt/C and carbon paper (Toray TGP-060) were purchased from E-TEK.

3.2.2 Preparation and Characterization of Pt DENs

In a typical preparation of Pt DENs, 500 µL of a 1 mM PAMAM G4 solution was dissolved in 4 mL deionized water in a quartz tube, followed by slowly adding 500 µL of 10 mM H$_2$PtCl$_6$ solution with bubbling N$_2$ to remove any dissolved O$_2$. Subsequently, the solution was UV irradiated for 48 h. The solution was dialyzed using a cellulose dialysis sack to remove impurities.

The UV–Vis absorbance spectra of the samples were recorded on a Cary 50 UV-Vis spectrophotometer (Varian, USA). The optical path length was 1.0 cm, and deionized water was used as reference. The chloride concentration of the sample was measured with a Chloridometer (Haake Buchler Instruments Inc NJ, USA). Transmission electron microscopy (TEM) images of the Pt DENs were obtained on a FEI TECNAI F20. The TEM samples were prepared as follows: the copper grid was first cast with a thin Nafion® film by floating it on the surface of a Nafion® solution for 30 min, and then dried in air. This copper grid was then floated on the surface of a Pt DEN solution for 30 min. After that, the copper grid was rinsed thoroughly with deionized water to remove loosely bound Pt DENs.

All electrochemical experiments were performed in a glass cell using a standard three-electrode configuration with a Pt-wire counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode (GCE) (BASi, MF-2012 3.0 mm dia.). GCEs were prepared by polishing with 1.0 and 0.05 µm alumina powder on a polishing
cloth (Buehler) followed by sonication in deionized water for 3 min. Then the electrodes were rinsed with water and dried under flowing \( \text{N}_2 \) gas. For convenience, measured potentials are reported versus the normal hydrogen electrode (NHE). Cyclic voltammetry was performed using a CHI660 electrochemical workstation (CH Instruments, Austin, TX).

### 3.2.3 Preparation and Characterization of Self-assembled MEA

Nafion\textsuperscript{®}-117 membrane, having equivalent weight of 1100 and thickness of 7 mil, was provided by DuPont. The membrane was cleaned and converted to acid form by using the following procedure: boiled in 2\% hydrogen peroxide for 1 h, rinsed with deionized water, then boiled in 0.5 M sulfuric acid for 1 h, washed thoroughly with deionized water, and stored in deionized water before use. The pretreated membrane was immersed in a Pt DEN solution for 1 hour to form a monolayer of Pt DENs on Nafion\textsuperscript{®} surface. The self-assembled MEA was rinsed thoroughly with deionized water.

Attenuated total reflection (ATR)-FTIR spectroscopy (JASCO FTIR-4100) was used to study the chemical structures of the self-assembled MEA. The spectra were collected by performing 128 scans for each sample at a resolution of 4 cm\(^{-1}\). A Digital Instrument Nanoscope IV-atomic force microscopy (AFM) (Digital Instruments, Veeco Metrology, Santa Barbara, CA) in tapping mode was used to image each sample in air at room temperature. The lateral scan frequency was 1 Hz. All images were recorded in a 512×512 pixel format. X-ray photoelectron spectroscopy (XPS) characterization of the samples was performed using a Kratos Analytical Axis 165 multitechnique spectrometer with a concentric hemispherical analyzer. Monochromatic Al K\(\alpha\) (1486.6 eV) was used for all measurements. The samples were analyzed at 90° take off angle.
A pass energy of 160 eV was used for the survey scan and 80 eV was used for the high resolution scan of the Pt(4f) peaks. Energy referencing was employed using the F1s peak located at 688.9 eV.\textsuperscript{19}

Proton conductivity measurements were carried out using an electrochemical workstation (Model CHI 660A) from CH Instruments in the frequency region from 1 Hz to $10^5$ Hz. A sample of membrane was fixed by four copper electrodes along a line, as shown in Figure 3.3. The gap width between adjacent electrodes is 1 cm. The two outside copper electrodes were connected to the working electrode (WE) and counter electrode (CE), which were used to feed current to the sample. The two inside copper electrodes were connected to the two reference electrodes (RE), which were used to measure the potential drop. The electrochemical cell was placed in a jacketed glass vessel as shown in Figure 3.4. Temperature was maintained at 20 °C, and the relative humidity was saturated at 100%. The proton conductivity $\sigma$ was measured in the longitudinal direction and calculated from the equation

$$\sigma = \frac{l}{RS}$$ [3.1]

Where $l$, $R$ and $S$ are the thickness, resistance and cross-sectional area of the membrane, respectively.

### 3.2.4 Immobilization of Pt DENs and Carbon Powder on Carbon Paper

To further improve the performance of the MEA, the immobilization of Pt DENs and carbon powder on carbon paper was carried out using procedures similar to those introduced in Section 3.2.2. Here, the working electrode is a piece of carbon paper. A cellulose sack is used to separate the electrolyte solution of the working electrode (0.1
Figure 3.3. Schematic drawing of electrochemical cell used to measure the proton conductivity of Nafion®.

Figure 3.4. Schematic drawing of apparatus for measuring proton conductivity.
M LiClO$_4$, 50 µM Pt DENs, and 0.02 g carbon powder) from that for the counter and reference electrodes (0.1 M LiClO$_4$), as shown in Figure 3.5. The cellulose sack confines Pt DENs and carbon powder surrounding the carbon paper, while allowing electrons to pass through freely. A control sample was prepared by scanning the same potential in a solution only containing 0.1 M LiClO$_4$ and 0.02 g carbon powder inside the cellulose sack. Both samples were sonicated in deionized water for 30 min and rinsed thoroughly with deionized water.

The morphology of the carbon paper was characterized by scanning electron microscopy (FE-SEM, JEOL 7000 F) operating at 20 KV.

3.3 Results and Discussion

3.3.1 Preparation and Characterization of Pt DENs

Formation of the Pt$^{4+}$/dendrimer complex is the first step of the dendrimer encapsulated nanoparticle synthesis. To determine the form of Pt$^{4+}$ that binds to the amide groups of the dendrimer, time-resolved UV−Vis analysis and chloride concentration study were carried out. Figure 3.6 shows time-resolved UV-Vis spectra obtained from 50 µM aqueous PtCl$_6^{2−}$ solutions. The top spectrum, taken immediately after solution preparation, reveals absorbance at 260 nm, which are characteristic of chloroplatinic ions. The intensity of these peaks decreases for ~10 h and then achieves a nearly constant value, which indicates that chloroplatinic ions diffuse slowly into the interior of PAMAM G4 to finish a ligand substitution reaction from Cl$^−$ to nitrogen of the dendrimer. To avoid aggregation, at least 10 hrs reaction before UV irradiation is necessary. The chloride concentrations measured by a chloridometer are shown in
Figure 3.5. Schematic drawing of immobilization of Pt DENs and carbon powder on carbon paper.

Electrolyte: 50 µM Pt DEN + 0.1 M LiClO$_4$ + 0.02 g carbon powder

Electrolyte: 0.1 M LiClO$_4$

Scan rate: 10 mV/s
Figure 3.6. Variation of UV-Vis absorption spectra of the solution containing PtCl$_6^{2-}$ as a function of time.
Figure 3.7. There are some free chloride ions in chloroplatinic acid solution due to hydrolysis. After the addition of PAMAM, in the first 50 minutes, the chloride concentration goes up rapidly, which is consistent with the UV-Vis absorption. After that, the increase rate of chloride concentration slows down. After 20 days, about 75% chloride can be detected by the chloridometer, which means ca. 75% chloride can be substituted by PAMAM dendrimer, and still 25% of chloride is bound with Pt. This result is similar to the NMR results reported for the complexation of $K_2PtCl_4$ with PAMAM dendrimers by Pellecchia’s group.$^{15}$ They found that as much as 20% of the Pt precursor may not be complexed to the dendrimer.

The UV-Vis spectra recorded during the photoreduction of Pt ions are shown in Figure 3.8. In the absence of dendrimer, the spectrum of $H_2PtCl_6$ has a strong absorbance peak at 260 nm arising from a ligand-to-metal charge transfer (LMCT).$^{11,20,21}$ When PAMAM is added to this solution, the peak at 260 nm decreases and shifts to 275 nm, which suggests some chloride ligands are replaced by amine ligands, and ligand field splitting of the Pt 5d orbital slightly expands due to a ligand substitution reaction from chloride to oxygen or nitrogen of the dendrimer, which provides a stronger ligand field than chloride.$^{22}$ After UV irradiation, the solution color changes from light yellow to golden brown. The new band located at 287 nm is assigned to certain carbonyl compounds formed by photodecomposition of the dendrimers.$^{22}$ The absorption at wavelengths >350 nm results from the interband transition of the encapsulated Pt nanoparticles.$^{23,24}$ The reduction process appears to complete within 48 hrs. After dialysis, the color of the solution changes from golden brown to brown.
Figure 3.7. Variation of chloride concentration as a function of time.
Figure 3.8. UV-Vis spectra during the photoreduction of Pt ions.
The Pt nanoparticles made by photoreduction were studied by TEM. A typical HRTEM image is shown in Figure 3.9. The Pt nanoparticles are highly monodisperse with an average size of 2.6 ± 0.4 nm in diameter. The high-resolution TEM image also shows that most of the nanoparticles have clear crystalline planes aligned along a specific direction. As such, nanoparticle ‘a’ has a lattice spacing of 0.226 nm, which corresponds to the (111) plane of Pt, while nanoparticle ‘b’ has a lattice spacing of 0.198 nm, which corresponds to the (200) plane of Pt. Therefore, one can conclude that the final products are indeed Pt nanoparticles. These Pt nanoparticles also exhibit good stability being attributed to the encapsulation inside the dendrimers. They remain dispersed in solution for at least several months.

The oxygen reduction reaction (ORR) is the great source of inefficiency in H$_2$-PEMFCs and DMFCs.$^{25,26}$ In order to study the electrocatalytic activity of the Pt DENs toward the ORR, the Pt DENs were immobilized on a GCE using the procedure reported by Deinhammer et al.$^{27}$ A freshly polished GCE was placed in an aqueous 50 µM Pt DENs solution containing 0.1 M LiClO$_4$, and then the potential of the electrode was scanned three times between 0.22 V and 1.62 V (vs. NHE). Figure 3.10a shows three CV background scans obtained in the supporting electrolyte solution, only a small background current is observed. However, in the presence of PAMAM (Figure 3.10b) or Pt DENs (Figure 3.10c), an irreversible wave appears. The current associated with this wave is mainly attributable to the one electron oxidation of the amine groups to its corresponding cation radical and the formation of a carbon-nitrogen linkage at the GCE surface, as shown in Figure 3.11.$^{27,28}$ After the first scan (solid curve), the current decreases and remains almost constant for the second and third scans (dash curve),
Figure 3.9. HRTEMs and size distribution plots for Pt DENs.
Figure 3.10. CVs obtained at a freshly polished GCE in (a) electrolyte solution only (b) electrolyte solution plus $10^{-4}$ M PAMAM, and (c) electrolyte solution plus $10^{-6}$ M Pt DENs. Scan rate: 10 mV/s.
which indicates that the maximal coverage can be obtained with a single voltage cycle between 0.22 V and 1.62 V. There are two possible explanations for the difference between these two waves related to the presence of PAMAM and Pt DENs. First, the diffusion rate of PAMAM and Pt DENs is different. Second, after dialysis, the concentration of Pt DENs is lower than that of PAMAM.

Figure 3. 11. Schematic illustration of the modification GCE with Pt DENs.

Figure 3.12 shows CVs for the reduction of $O_2$ at a bare GCE, a GCE modified with PAMAM, and a GCE modified with Pt DENs. All CVs were obtained in an $O_2$ saturated 0.5 M $H_2SO_4$ solution. Reduction at the bare GCE starts at a potential of ca. 0.12 V, and the peak at -0.18 V can be attributed to the reduction of water. The electrochemical behavior at a GCE modified with PAMAM is similar to that of a bare GCE. However, the Pt DENs modified GCE shows an onset current of ca. 0.72 V and a well-defined peak at 0.36 V; this oxygen reduction peak for the Pt DENs demonstrates that oxygen is able to penetrate the PAMAM, react on the Pt nanoparticle, and that the product of the reaction is able to escape the PAMAM.

In order to compare the activity of Pt DENs with that of commercial Pt nanoparticle catalyst (20 wt% Pt/C E-TEK), it is necessary to measure the loading of the Pt DENs and commercial Pt/C on GCE. One of the accepted methods for estimating the loading of Pt catalyst is H-adsorption/desorption. Pt DENs were immobilized on GCE by using the electrocoupling method introduced before. To estimate the loading, the electrode
Figure 3.12. CVs for the reduction of O$_2$ using (a) a bare GCE; (b) a GCE modified with PAMAM, and (c) a GCE modified with Pt DENs. Scan rate: 20 mV/s.
was placed in a 0.5 M H$_2$SO$_4$ solution, and the solution was degassed by bubbling N$_2$ for 30 min and protected with a nitrogen atmosphere during the entire experimental procedure. Figure 3.13 shows CV of Pt DENs modified GCE. The peaks between 0.05 and 0.3 V are characteristic of hydrogen adsorption and desorption. After subtraction of the background charge, the total charge is 2.5 µC, which corresponds to 0.012 cm$^2$ of surface area assuming that H$_2$ desorption yields 210 µC/cm$^2$ of Pt surface area. The Pt loading on the electrode is ca. 0.011 µg, assuming that all nanoparticles are spherical with a diameter of 2.6 nm. However, if there is a monolayer on the GCE surface, the Pt loading is supposed to be 0.24 µg, which indicates only ca. 4.5% of the surface of the GCE is covered by Pt DENs. The commercial Pt catalyst layer on GCE was obtained in the following way: (i) mix 3 mg Pt/C and 3 mL of 0.5% Nafion® solution, (ii) pipet 1 µL of the mixture and spread on the disk, and (iii) the electrode is then dried in air. The loading of commercial Pt is 2 µg.

Compared to commercial Pt nanoparticle catalysts (dash curve), the oxygen reduction current of the Pt DENs (solid curve) is about 2.3 times higher, as shown in Figure 3.14. There are three possible reasons. First, because photoreduction is a slow process, the Pt DENs may have less surface defects. It was reported that ORR occur preferentially on defect-free terraces; secondly, Pt DENs are smaller than the commercial Pt nanoparticles. The smaller the nanoparticle, the higher the surface area is; thirdly, Pt DENs may be more accessible to O$_2$. The current intensity is proportional to the local O$_2$ concentration. However, the overpotential is ~0.3 V greater. A possible reason for this is electron tunneling from the nanoparticle to the electrode due to the presence of nitrogen ligands from the dendrimer.
Figure 3.13. CV for Pt DENs modified GCE showing H-adsorption/desorption. Scan rate: 50 mV/s.
Figure 3.14. Linear sweep voltammograms for the reduction of O$_2$ using Pt DENs (solid curve) and Pt/C (dash curve). Scan rate: 50 mV/s.
The catalytic activities of Pt DENs (solid curve) against methanol oxidation were also measured and compared with that of commercial Pt/C (dash curve), as shown in Figure 3.15. The electrolyte is 2 M CH$_3$OH and 1 M H$_2$SO$_4$ mixture. Pt DENs are totally inert to methanol oxidation, while commercial Pt/C shows high methanol oxidation activity. The possible explanation is that the exterior of PAMAM G4 dendrimer is dense, and the space between the terminal groups acts as a gate to only allow small molecules in. Methanol is relatively large compared to oxygen, so it is not easily accessible to the Pt catalyst. This result implies a significantly new, patentable potential application of Pt DENs for the cathode in a DMFC.

3.3.2 Self-assembled MEA and Loading Enhancement

The self-assembled MEA was prepared by dipping the Nafion$^\text{®}$ membrane into a Pt DENs solution and then rinsing the assembly thoroughly with deionized water. Figure 3.16 shows the FTIR spectrum of a MEA. The amide band I (C=O stretching) centered at 1645 cm$^{-1}$ and amide band II (C-N bending) at approximately 1550 cm$^{-1}$ are characteristic of the dendrimer branches,$^{31}$ which indicates that the dendrimer is present on the surface. The 1200-1350 cm$^{-1}$ region is mainly attributed to the antisymmetric stretches of CF$_2$, and remains essentially unchanged compared to Nafion$^\text{®}$. The decrease in the vibrational frequency of SO$_3^-$ group from 1054 cm$^{-1}$ to 1048 cm$^{-1}$ can be attributed to a depolarization of the sulfonate group,$^{32}$ which suggests the electrostatic association of the Nafion$^\text{®}$ with the dendrimer.

XPS measurements confirm the presence of both the dendrimer and Pt on the Nafion$^\text{®}$. Figure 3.17a shows the XPS spectrum of the self-assembled MEA. The N(1s) peak at 399.8 eV confirms the existence of the PAMAM dendrimers, while the Pt(4d)
Figure 3.15. CVs for the oxidation of CH$_3$OH using Pt DENs (solid curve) and Pt/C (dash curve). Scan rate: 50 mV/s.
Figure 3.16. ATR-FTIR of the self-assembled MEA (dash curve) and Nafion® (solid curve).
Figure 3.17. (a) XPS spectrum of the self-assembled MEA. (b) High-resolution XPS spectrum in the Pt(4f) region.
and Pt(4f) peaks confirm the existence of Pt. The Pt(4f$_{5/2}$) and Pt(4f$_{7/2}$) peaks are located at 75.2 eV and 71.9 eV, respectively, which are higher compared to the binding energy reported for bulk Pt [74.6 eV for Pt(4f$_{5/2}$) and 71.2 eV for Pt(4f$_{7/2}$)]. However, this result is close to the observation by Ye et al.,$^{10}$ and it is possibly a consequence of the presence of the dendrimer and the small size of these nanoparticles.$^{14,33,34}$

Figure 3.18 shows AFM images of the self-assembled MEA and their corresponding TEM images of nanoparticles. The Pt DENs with a high degree of monodispersity (image b) were prepared with 24 hrs of reaction prior to UV irradiation. The MEA surface is smooth when these Pt DENs are doped on it, as shown in image a. The AFM image of this MEA is smooth due to low lateral resolution of AFM. AFM is accurate only when the tip curvature diameter is smaller than the particle diameter and the distance between particles. However, as shown in the image d, the Pt DENs were prepared with no reaction time prior to UV irradiation; the diameter of most of the Pt DENS clusters is more than 20 nm, a value considerably larger than the diameter of Pt DENs. It reveals that some aggregation exists. The AFM result (image c) is consistent with the TEM image (image d). A possible reason for this is some Pt$^{4+}$ might bind primary amine groups instead of the interior tertiary amines, inducing crosslinking of the dendrimers. Therefore, in order to obtain monodispersed nanoparticles, it is important to allow enough time for the hexacholoroplatinic acid to diffuse into the interior of the PAMAM before UV irradiation.

In order to observe the distribution of Pt DENs on the surface of Nafion$^\text{®}$ membrane, a specific TEM sample was prepared as follows: a thin Nafion$^\text{®}$ membrane was first coated on the copper grid; then the Pt DENs were attached onto the Nafion$^\text{®}$ membrane.
Figure 3.18. (a) AFM image of an MEA made with Pt DENs; (b) TEM image of Pt DENs; (c) AFM image of an MEA made with Pt DEN aggregates; (d) TEM image of Pt DEN aggregates.
by floating the copper grid on the surface of a Pt DENs solution. Figure 3.19 shows the TEM image of the self-assembled Pt DENs on Nafion®️, and the distribution of the self-assembled Pt DENs on Nafion®️ is uniform. Based on the TEM image, it was estimated that ca. $9 \times 10^{12}$ Pt nanoparticles per centimeter squared were made for the self-assembled MEA. Assuming that all nanoparticles are spherical in shape with the same diameter of 2.6 nm, the loading was about 2 µg/cm², which corresponds to ~48% coverage on the Nafion®️ surface.

A Pt loading of 2 µg/cm² is lower than that required for a reasonable performance of fuel cell. Two routes were proposed to increase the Pt loading, as indicated in the following section.

First, layer-by-layer self assembly. Layer-by-layer self assembly, fabrication of multilayers by consecutive adsorption of polyanions and polycations, was first developed by Decher et al.³⁵ This technique is simple, efficient, and has been used for PEMFC recently.²⁰,³⁶-³⁹ Figure 3.20 shows UV-Vis spectra of the layer-by-layer self-assembled Nafion®️ as a function of the number of Pt DENs layers. The overall absorbance attributed to the interband transition of Pt nanoparticles increases with the number of Pt DEN layers. To evaluate the effect of Pt DENs on the proton conductivity of Nafion®, the conductivity was measured, as shown in Figure 3.21. The conductivity of Nafion®️ is 0.073 S cm⁻¹, after 1 layer of Pt DENs self assembly, the proton conductivity decreased ca. 16%. Nevertheless, with an increase in the number of Pt DENs layers, the conductivity of the membrane remains almost the same. A possible explanation is that the PAMAM may serve as a proton conductor. In order to reach the
Figure 3.19. TEM image of the self-assembled MEA.
Figure 3.20. UV-Vis spectra of Nafion® as a function of the number of Pt DENs layers.
Figure 3.21. Proton conductivity of Nafion® as a function of the number of Pt DENs layers.
required Pt loading, ca. 80 layers Pt DENs are necessary, which could be accomplished by using a dipping machine.\textsuperscript{40}

Secondly, electrochemical impregnation of Pt DENs on carbon fibers. This method is based on the electro-oxidation of terminal amines on PAMAM to form several carbon-nitrogen linkages to the carbon surface. The working electrode is a piece of carbon paper. A cellulose sack is used to separate the electrolyte solution for the working electrode (0.1 M LiClO$_4$, 50 $\mu$M Pt DENs and 0.02 g carbon powder) from that for the counter and reference electrode (0.1 M LiClO$_4$). The cellulose sack confines Pt DENs and carbon powder surrounding the carbon paper, while allowing electrons to pass through freely. A control sample was prepared by scanning the same potential in a solution only containing 0.1 M LiClO$_4$ and 0.02 g carbon powder inside the cellulose sack. Both samples were sonicated in deionized water for 30 min and rinsed thoroughly with deionized water. Even more, carbon powder was added into the system, if the carbon powder can also be attached to the carbon paper, the electron transfer efficiency would be further improved. It was measured that the surface area of carbon paper is ca. 0.01 m$^2$/g, while the surface area of carbon powder can reach 250 m$^2$/g.

Figure 3.22a shows three CV background scans obtained in the mixture of supporting electrolyte solution and carbon powder, only a small background current is observed. However, in the presence of Pt DENs (Figure 3.22b), several irreversible waves appear, indicating the formation of carbon-nitrogen linkages and the introduction of Pt DENs on the carbon fiber. These irreversible waves do not indicate that there is a multi-electron reaction; it is still a one-electron reaction. The possible reasons are that the carbon paper is porous and some impurity in the carbon paper might get oxidized.
Figure 3.22. CVs obtained at carbon paper in (a) electrolyte solution only (b) electrolyte solution plus 10^-4 M Pt DENs and carbon paper. Scan rate: 10 mV/s.
CVs for the reduction of \( \text{O}_2 \) at carbon paper, and carbon paper modified with Pt DENs are shown in Figure 3.23. All CVs were obtained in an \( \text{O}_2 \) saturated 0.5 M \( \text{H}_2\text{SO}_4 \) solution. Only a small background was observed for the carbon paper. However, the Pt DENs modified carbon paper shows a well-defined oxygen reduction peak. Even more, because the Pt nanoparticles are chemically attached to the carbon paper, no aggregation would occur.

In order to test the stability of the combination of carbon fiber, Pt DENs, and carbon power, the carbon paper modified with Pt DENs and carbon powder by electrochemical coupling was sonicated for 30 min, and then rinsed with DI water thoroughly. After that, the SEM image was obtained and compared to the two controls (carbon paper only and carbon paper modified with carbon powder), as shown in Figure 3.24. Clearly, a large amount of carbon powder is strongly attached onto the carbon paper even after 30 min of sonication. The SEM images of the carbon paper and the carbon paper modified with only carbon powder are smooth. The Pt DENs function as a "glue" for the carbon powder and carbon paper. Introduction of carbon powder should provide an improved electronic pathway, inducing higher electron conductivity.

It is reported that the surface area of a carbon nanofiber can reach as high as 2350 m\(^2\)/g.\(^40\) Thus, the Pt loading could be estimated at ca. 0.2 gram Pt per gram carbon nanofibers based on the loading on a GCE, which would be enough for fuel cell applications. The electrocoupling is an easy and very efficient way to attach Pt nanoparticles and carbon powder onto carbon paper.
Figure 3.23. CVs for the reduction of O$_2$ using (a) carbon paper; (b) the carbon paper modified with Pt DENs and carbon powder. Scan rate: 20 mV/s.
Figure 3.24. SEM images of (a) the control; (b) the carbon paper modified with carbon powder; (c) the carbon paper modified with Pt DENs and carbon powder.
3.4 Conclusions

Pt DENs have been successfully synthesized using photoreduction. The nanoparticles are highly monodisperse with an average of 2.6 nm in diameter. These nanoparticles exhibit a high specific activity for the oxygen reduction reaction and are inert to methanol oxidation reaction, showing great potential for application in PEMFC and DMFC. This is a novel and potentially patentable result! A simplified MEA has been fabricated by the electrostatic self-assembly between Nafion® and Pt DENs. Two methods were proposed to increase Pt loading: layer-by-layer self assembly and immobilization of Pt DENs onto carbon paper. Approximately 80 layers are proposed to reach the required loading using a dipping machine. Immobilization of Pt DENs and carbon powder simultaneously on a carbon nanofiber can easily reach the required Pt loading for fuel cells, which makes this a very promising method with which to replace the conventional method of electrode fabrication.
3.5 References


CHAPTER 4

MODIFICATION OF NAFION® WITH PAMAM G0 FOR DIRECT METHANOL FUEL CELLS

4.1 Introduction

Direct methanol fuel cells (DMFCs) are promising power sources due to the simplicity of the system and the adaptability of the liquid fuel, methanol. One of the main impediments to the practical realization of the DMFC is the crossover of the methanol through the polymer electrolyte membrane from the anode to the cathode. Currently, the most common polymer electrolyte used in a fuel cell is Nafion® because of its good chemical, physical and thermal stability as well as high proton conductivity under high humidity conditions. However, in DMFCs, due to similar properties of methanol compared to water, methanol molecules as well as water molecules are transported through Nafion® from the anode to the cathode of the cell by electro-osmotic drag as well as by diffusion. It has been reported that up to 40% of the methanol can be wasted in DMFCs across Nafion®. Moreover, at the cathode, methanol causes a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction, resulting in low cell performance. Therefore, it is very important to reduce the methanol crossover of Nafion® membrane to make it a qualified candidate for DMFC applications.

Intense research has been focused on reducing the methanol permeability of the Nafion® membrane.
Impregnating polymers within membranes is a strategy to reduce the methanol permeability. Smit et al.\textsuperscript{3} studied the modification of Nafion\textsuperscript{®} by \textit{in situ} polymerization of pyrrole. This procedure included immersing Nafion\textsuperscript{®} in an electrolyte containing the monomer and then polymerizing within the membrane galvanostatically in an electrochemical cell. The polypyrrole doped Nafion\textsuperscript{®} membranes exhibited a lower methanol permeation, but no proton conductivity was reported. Sungpet\textsuperscript{4} reported that the incorporation of poly(pyrrole) within Nafion\textsuperscript{®} membranes with \textit{in situ} polymerization using peroxide as the free radical initiator resulted in decreased methanol and water sorption. However, no methanol permeability and proton conductivity data were reported. Park \textit{et al.}\textsuperscript{5} impregnated Nafion\textsuperscript{®} membranes with poly(pyrrole) using \textit{in situ} polymerization and observed an approximate 5 times increase in selectivity compared to Nafion\textsuperscript{®}. Bae \textit{et al.}\textsuperscript{6} impregnated poly(1-vinylimidazole) within a Nafion\textsuperscript{®} membrane and observed a 25\% increase in both methanol permeability and proton conductivity compared to Nafion\textsuperscript{®}. Liu \textit{et al.}\textsuperscript{7} impregnated Nafion\textsuperscript{®} membranes with poly(furfuryl alcohol) and observed improved DMFC performance with a maximum power density \textasciitilde180\% higher than Nafion\textsuperscript{®} and higher cell voltages at all current densities.

Incorporating micrometer to nanometer size filler, such as, silica, titanium oxide, layered silicate nanoparticles, into Nafion\textsuperscript{®} is another strategy to reduce the methanol permeability. Antonucci \textit{et al.}\textsuperscript{8} prepared a Nafion\textsuperscript{®}-silica composite membrane with lower methanol permeation than Nafion\textsuperscript{®}, and the operation temperature can reach 145 °C, however, the fuel cell performance decreased. Montmorillonite was also chosen as a filler by several groups due to the ability to enhance the mechanical properties of the membrane and its ion conductivity. Song \textit{et al.}\textsuperscript{9} mixed montmorillonite
with Nafion® and solvent cast the mixture into membranes. The solvent cast membrane has ~20% higher proton conductivity and ~20 times less methanol permeability compared to Nafion®. Jung et al.\textsuperscript{10} used pulverization, mixing and heat pressing to produce a composite membrane that has low conductivities. Permeability data were inconclusive because their methods were incomparable to other standard experimental methods.

Coating Nafion® with thin barrier layers is also utilized to reduce methanol crossover. Yoon et al.\textsuperscript{11} prepared a homogeneous palladium film on Nafion® membrane via sputter coating. The methanol permeability decreased by an order of magnitude, while the proton conductivity decreased only slightly. Li et al.\textsuperscript{12} fabricated a nano silica coated Nafion® composite via plasma enhanced chemical vapor deposition. Methanol permeability decreased 67%. However, DMFC tests reveal a lower performance. Low dose electron beam exposure has also been used to modify the surface of Nafion® membrane. DMFC tests show higher power densities after exposure.\textsuperscript{13} Shao et al.\textsuperscript{14} coated PVA on both sides of a Nafion® membrane using an immersion technique. That resulted in a 61% increase in selectivity.

This chapter focuses on the modification of commercial Nafion® membranes by impregnating them with PAMAM G0 dendrimers. The diameter of the ionic clusters in Nafion® is about 3-10 nm, which was demonstrated by both small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).\textsuperscript{15,16} The channels between the clusters are narrower than the clusters. Although PAMAM G0 dendrimers are reported to be 1.5 nm in diameter, their planar structure provides the possibility of PAMAM G0 dendrimers squeezing into the Nafion® membrane to change the structure of the
channels and clusters by crosslinking. It is known that methanol predominantly diffuses through hydrophilic ionic channels and clusters of the membranes, while protons primarily permeate by hopping between ionic sites. Thus, the methanol permeability strongly depends on the cross-sectional size of the ionic channels and clusters, but the proton conductivity does not.\textsuperscript{17} Therefore it is expected that introducing PAMAM G0 into the ionic channels and clusters should reduce the methanol permeability, while the proton conductivity should be virtually unchanged. Besides that, the amino groups in PAMAM may act as additional sites for proton transport through the membrane,\textsuperscript{18} which might help maintain high proton conductivity.

4.2. Experimental

4.2.1 Materials

Nafion\textsuperscript{®}-117 membrane, having an equivalent weight of 1100 and thickness of 7 mil, was provided by DuPont. Amine-terminated generation zero poly(amidoamine) (PAMAM-NH$_2$ G0) was obtained as a 10\% methanol solution (Aldrich-Sigma). Prior to use, the methanol was removed under vacuum at room temperature. Deionized water (18 MΩ-cm Milli-Q) was used to prepare aqueous samples. Hydrogen peroxide, sulfuric acid, silver nitrate, methanol, iso-butanol and sodium borohydride were purchased from Aldrich-Sigma.

4.2.2 Preparation and Characterization of PAMAM G0 Doped Nafion\textsuperscript{®} Membranes

DuPont’s Nafion\textsuperscript{®} 117 membranes were cleaned and modified into the acid form by using the following procedure: boiled in 2\% hydrogen peroxide for 1 h, rinsed with deionized water, followed by boiling in 0.5 M sulfuric acid for 1 h and washing
thoroughly with deionized water. Then small pieces of Nafion® membrane were immersed in a weighing bottle filled with 10.0 mL of PAMAM G0 solution of known concentration for 24 h and rinsed thoroughly with water. The doped membranes were stored in deionized water.

The surface functional groups of the un-doped and doped membranes were determined using X-ray photoelectron spectroscopy. Monochromatic Al Kα (1486.6 eV) was used for all measurements. The samples were analyzed at a 90° take off angle. A pass energy of 160 eV was used for the survey scan, and 80 eV was used for the high-resolution scan of the C1s, F1s, O1s, N1s, and S2p peaks. Energy referencing was employed using the F1s peak located at 688.9 eV.\textsuperscript{12}

In order to investigate the change of structure inside the Nafion® after treatment with PAMAM G0, Ag nanoparticles were prepared using Nafion® as the template. In a typical experiment, a piece of pretreated Nafion® film was soaked in an aqueous 0.1 M silver nitrate solution for 30 min. Then, the membrane was rinsed with deionized water thoroughly and soaked in a freshly prepared 0.2 M sodium borohydride solution for 2 min.

Specimens for TEM were prepared by a method in which 3 mm discs were punch cut from the thin films using a South Bay Technology punch cutter. The discs were then dimpled to a thickness of 20 µm by a dimpler made by South Bay Technology. During dimpling a strip of 600-grid silicon carbide paper was glued to the polishing wheel of the dimpler for smooth and slope free polishing. The dimpled specimens were then ion milled to a thickness of 100 nm or less to allow electron beam transmission.

The proton conductivity measurements were carried out using the same procedure
Methanol permeability of the samples was measured using a two-compartment diffusion cell.\textsuperscript{19} One compartment of the cell (compartment A) was filled with the solution of methanol (8.0 vol %) and iso-butanol (0.2 vol %) in deionized water. The other compartment (compartment B) was filled with an iso-butanol (0.2 vol %) solution in deionized water. The membrane was clamped between the two compartments that were continuously stirred during permeability measurement. The ratio of methanol to iso-butanol peak area in compartment B was measured by GC/FID and converted to a methanol concentration using a calibration curve. The methanol concentration in compartment B as a function of time is given by

\[ C_B = \frac{APC_A(t-t_0)}{V_BL} \]  \[ 4.2 \]

where \( C \) is concentration, \( A \) and \( L \) are the membrane area and thickness, \( P \) is the methanol permeability. The concentration of methanol in compartment B was plotted versus time. The methanol permeability was estimated from the slope of the plot.

An Agilent 6890 GC with an FID detector was used to measure the methanol concentration in compartment B. The EC\textsuperscript{TM}-WAX column coated with a polyethylene glycol stationary phase can separate methanol and iso-butanol very well. The operating parameters for the method are summarized in Table 4.1. A calibration curve (Figure 4.1) was obtained as follows: 1) a series of standard solutions of methanol in deionized water with fixed concentrations of iso-butanol were prepared and injected into the GC in sequence; 2) the ratio between methanol and iso-butanol for each standard sample was calculated from the chromatogram; 3) a plot of the y-axis as the ratio between methanol and iso-butanol and the x-axis as the known methanol concentration was obtained.
Table 4.1 GC parameters for the measurement of methanol crossover.

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<tr>
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Figure 4.1. GC calibration curve.
4.2.3 Fabrication of the MEA and Fuel Cell Performance Measurement

The MEAs were fabricated by using the Nafion® 117 membrane via a conventional hot-press method. The commercial E-TEK electrodes were employed as both anode [5 mg/cm² loading using unsupported HP Pt:Ru (nominal atomic ratio of 1:1)] and cathode (5 mg/cm² loading using unsupported HP Pt Black). The MEAs with an active area of 5.0 cm² were fabricated by sandwiching either a doped or un-doped Nafion® membrane between the anode and cathode, then hot pressing them at 160 °C under a pressure of 300 lb for 150 sec. The obtained MEA was carefully installed between two sealing gaskets, and then two graphite plates. The MEAs were conditioned with humidified H₂/air as PEMFC for about 50-60 hours at 60 °C before switching to measure the DMFC polarization curves. These tests were performed on fuel cell test system 890 B from Scribner Associates Inc.

The DMFC performance test was conducted at 60 °C by feeding different concentrations of aqueous methanol (1 M, 2 M, 5 M) at a flow rate of 3.0 mL/min using a micro-pump and by feeding dry oxygen gas to the cathode at a flow rate of 100 mL/min at ambient pressure. Polarization data were recorded by applying a constant current from a potentiostat. The voltage at each current was recorded after stabilization for 3 min.

4.3 Results and Discussion

4.3.1 Characterization of PAMAM G0 Doped Nafion® Membrane

The control Nafion® membranes and PAMAM G0 (10⁻³ M and 10⁻⁵ M) doped Nafion® membranes were characterized using XPS. The XPS survey spectra of these
membranes, as shown in Figure 4.2, reveal the presence of fluorine, oxygen, carbon and sulfur in the Nafion® membrane. After $10^{-3}$ M PAMAM G0 treatment, a nitrogen peak at ca. 400 eV was also observed. The O(1s) spectra of the un-doped and doped Nafion® are shown in Figure 4.3. In the control, the peak at higher binding energy (ca. 536 eV) corresponds to the oxygen atoms in a fluoroether environment; the peak at lower binding energy (ca. 534 eV) is related to the oxygen atoms in the sulfonic acid groups. After $10^{-3}$ M PAMAM G0 treatment, a new peak at ca. 532 eV that corresponds to the carboxyl group in PAMAM appeared. After $10^{-6}$ M PAMAM G0 treatment, no obvious peak at ca. 532 eV can be observed due to the detection limit of XPS.

The N(1s) spectra of the un-doped and doped Nafion® are shown in Figure 4.4. After PAMAM G0 treatment, two nitrogen peaks show up. As the concentration of PAMAM G0 increases, the intensities of the peaks increase. The peak at higher binding energy (ca. 402 eV) corresponds to protonated nitrogen atoms due to the presence of sulfonic acid groups in the Nafion® membrane. The peak at lower binding energy (ca. 400 eV) is related to unprotonated nitrogen in PAMAM.

The C(1s) spectra of the undoped and doped Nafion® are shown in Figure 4.5. For the control Nafion®, the peak at ca. 292 eV is related to the superposition of the signals from fluorocarbons. After $10^{-3}$ M PAMAM G0 treatment, two new carbon peaks appeared. The peak at ca. 288 eV corresponds to the carbon atoms in the carboxyl groups in PAMAM. The peak at ca. 286 eV is related to the carbon atoms in C-N bonds in PAMAM.
The S(2p) spectra of the undoped and doped Nafion® are shown in Figure 4.6. After PAMAM G0 treatment, the S(2p) peak shifts to lower binding energy, which further confirms the presence of ammonium-sulfonate pairs.

Figure 4.2. XPS spectra of doped and undoped Nafion®.
Figure 4.3. High-resolution spectra in the O(1s) region.
Figure 4.4. High-resolution spectra in the N(1s) region.
Figure 4.5. High-resolution spectra in the C(1s) region.
Figure 4.6. High-resolution spectra in the S(2p) region.
In order to investigate the change of structure inside the Nafion® after treatment with PAMAM G0, Ag nanoparticles were prepared using Nafion® as the template. Direct TEM imaging of the Nafion® embedded with nanoparticles can provide new insight into the Nafion® structure.\textsuperscript{21}

The formation of silver nanoparticles in the Nafion® membranes can be monitored by UV-Vis. Figure 4.7 is a typical UV-Vis spectrum of Nafion® membrane embedded with Ag nanoparticles. The band at ca. 400 nm is the characteristic surface plasmon absorption of silver nanoparticles.\textsuperscript{22}

![Figure 4.7. The UV-Vis absorption spectrum of silver nanoparticles in Nafion® membrane.](image)

Both the size and distribution of the nanoparticle were further analyzed by TEM. Figure 4.8 shows the TEM images of Ag nanoparticles inside the Nafion® membrane: a) un-doped Nafion®; b) Nafion® doped with $10^{-4}$ M PAMAM; and c) Nafion® doped with
$10^{-2}$ M PAMAM, and the corresponding statistical analysis of nanoparticle sizes. Clearly, the silver nanoparticles embedded in Nafion® membrane are close to being spherical in shape. The average size of these Ag nanoparticles is 15.9 nm in diameter, with the standard deviation of the size distribution being 1.6 nm. However, the observed Ag nanoparticles are larger than the results reported by Fujimura et al.$^{15,16}$ A possible explanation is that the hydrophilic cavities and channels are flexible to accommodate the large Ag nanoparticles. More interestingly, the average size of Ag nanoparticles decreased to 7.8 nm for $10^{-4}$ M PAMAM doped Nafion®, and 2.9 nm for $10^{-2}$ M PAMAM doped Nafion®, which indicates that PAMAM G0 can penetrate into the bulk of Nafion® through cluster channels. Because there are four terminal amine groups in each PAMAM G0 dendrimer, these dendrimers may re-organize the distribution of sulfonate clusters by interacting with the sulfonic acid groups in different clusters, causing the hydrophilic cavities to shrink. The extent of shrinkage increases as the concentration of PAMAM G0 goes up. In theory, the shrinkage of hydrophilic cavities will reduce the methanol permeability.

Methanol permeability of the Nafion® was determined using the permeation cell. The methanol concentration in the receiving compartment, which was determined by GC, increased linearly with time as shown in Figure 4.9. The methanol permeabilities in the membranes can be calculated from the slopes of the linear fitting lines using Equation 4.2. As shown in Table 4.2, PAMAM dendrimer treatment can decrease the methanol permeability of Nafion® membrane, and the higher concentration the PAMAM G0, the lower the methanol permeability is. This result is consistent with the TEM
Figure 4.8. The TEM images of Ag nanoparticles inside the Nafion® membrane: (a) undoped Nafion®, (b) Nafion® doped with $10^{-4}$ M PAMAM; and (c) Nafion® doped with $10^{-2}$ M PAMAM, and the corresponding statistical analysis of nanoparticle sizes.
Figure 4.9. Concentration vs. time of methanol permeated through doped and un-doped membranes.

Table 4.2 Methanol permeability of doped and un-doped Nafion® membranes.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Methanol permeability (×10^6 cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>2.67 ± 0.04</td>
</tr>
<tr>
<td>Nafion®-PAMAM G0 10^{-6} M</td>
<td>2.05 ± 0.04</td>
</tr>
<tr>
<td>Nafion®-PAMAM G0 10^{-5} M</td>
<td>1.75 ± 0.08</td>
</tr>
<tr>
<td>Nafion®-PAMAM G0 10^{-4} M</td>
<td>0.87 ± 0.05</td>
</tr>
<tr>
<td>Nafion®-PAMAM G0 10^{-3} M</td>
<td>0.73 ± 0.09</td>
</tr>
</tbody>
</table>
images of Ag nanoparticles embedded Nafion® membranes. The average diameter of cavities inside the Nafion® decreases following the same trend, which provides the evidence of that methanol predominantly diffuses through hydrophilic cavities of the membranes and reducing the size of cavities can decrease the methanol permeability.

The proton conductivities of Nafion® membranes were measured by the four-probe AC impedance spectroscopy method. Using a Bode plot, the resistance of the membrane was obtained from the intercept of the signal, which was then converted to the proton conductivity by using Equation 3.1. The proton conductivities of PAMAM G0 doped and undoped Nafion® membranes are shown in Figure 4.10. For Nafion®, the proton conductivity is 0.073 S/cm, which agrees well with literature values. Treatment with $10^{-6}$ M PAMAM G0 decreased the proton conductivity from 0.073 S/cm to 0.052 S/cm. When the concentration of PAMAM G0 dendrimer is increased to $10^{-5}$ M and $10^{-4}$ M, the proton conductivity continues to decrease slightly. However, if the concentration of PAMAM G0 is increased to $10^{-3}$ M, there is a significant decrease in proton conductivity. One possible explanation is crosslinking between PAMAM G0 and Nafion® significantly shrinks the cavities of the Nafion® membrane and reduces the water content of the membrane to a critical point. Even the presence of a large number of amine groups cannot compensate for the loss of proton conductivity due to membrane dehydration. In order to validate this explanation, relative water uptake was determined by the weight increase upon equilibration in deionized water. The wet weight ($W_{\text{wet}}$) was measured immediately after removing residual water from the film surfaces. The membrane dry weight ($W_{\text{dry}}$) was obtained after drying at 50 °C for 2 h. The percentage of relative water uptake was calculated using
Figure 4.10. Proton conductivity of doped and un-doped Nafion® membranes.
Relative water uptake% = \( \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \).

Relative water uptake is ca. 25% for Nafion®. However, for the Nafion® treated with 10^{-3} M PAMAM G0, the relative water uptake is only 13%.

To a great extent, the DMFC performance is determined by the membrane’s balance between proton conductivity and methanol permeability. The trade-off between proton conductivity and methanol permeability can be described by selectivity. In Figure 4.11, the selectivity, also the ratio of proton conductivity to methanol permeability, is shown for the PAMAM G0 doped and un-doped Nafion® membranes. Nafion® treated with 10^{-4} M PAMAM G0 shows a higher selectivity than does the Nafion® control, which indicates 10^{-4} M PAMAM G0 treated Nafion® might give better performance.

4.3.2 Fuel Cell Performance Measurement

The polarization curve, which represents the relationship between the cell voltage and current density, is the most important performance test for fuel cells. The data is obtained by incrementally increasing the current density starting from zero. A plot of voltage versus current density, scaled by the geometric area of the electrode, gives results that are scalable. An alternative way of showing this data is as a plot of power density versus current density. Power density is simply the product of the voltage and the current density. \(^{23}\)

Figure 4.12 shows the polarization curves of MEAs made from un-doped and doped Nafion® using 1.0 M aqueous methanol. It can be seen that at a potential of 0.4 V, the current densities of membranes: control, treated with 10^{-6} M PAMAM G0, 10^{-5} M PAMAM G0, and 10^{-4} M PAMAM G0 are 167, 186, 204, and 259 mA/cm^2, respectively. Their maximum power densities are 77, 82, 87 and 105 mW/cm^2, respectively. The
Figure 4.11. Selectivity for doped and un-doped Nafion® membranes.
Figure 4.12. Polarization curves for the MEA made from un-doped and doped Nafion® at 60 °C with 1 M aqueous methanol.
performance of the MEA increased with increasing PAMAM G0 concentration from \(10^{-6}\) M to \(10^{-4}\) M. The MEA made with \(10^{-4}\) M PAMAM G0 treated Nafion\textsuperscript{®} membrane has a \(\sim 136\%\) maximum power density compared to the MEA made with Nafion\textsuperscript{®} membrane. This result is roughly consistent with the selectivity. The Nafion\textsuperscript{®} membrane treated with \(10^{-4}\) M PAMAM G0 has the highest selectivity and also shows the best fuel cell performance, although it has a lower proton conductivity than Nafion\textsuperscript{®} (un-doped) does. However, no polarization curves could be obtained from Nafion\textsuperscript{®} treated with \(10^{-3}\) M PAMAM G0 due to its low proton conductivity.

Figure 4.13 shows the polarization curves for un-doped and doped Nafion\textsuperscript{®} when 2.0 M aqueous methanol is used. At a potential of 0.4 V, the current densities of membranes: control, treated with \(10^{-6}\) M PAMAM G0, \(10^{-5}\) M PAMAM G0, and \(10^{-4}\) M PAMAM G0 are 181, 219, 235, and 298 mA/cm\(^2\), respectively. The MEA shows better performance at 2.0 M methanol than at 1.0 M methanol. Again, the performance of the MEA was increased with increasing the PAMAM G0 concentration from \(10^{-6}\) M to \(10^{-4}\) M. At 2.0 M methanol, the MEA made with \(10^{-4}\) M PAMAM G0 treated Nafion\textsuperscript{®} membrane has a \(\sim 165\%\) maximum power density compared to the MEA made with Nafion\textsuperscript{®} membrane.

However, when 5.0 M aqueous methanol was fed into the fuel cell system, the fuel cell performance went down, as shown in Figure 4.14. At a potential of 0.4 V, the current densities of MEAs made with membranes: control, treated with \(10^{-6}\) M PAMAM G0, \(10^{-5}\) M PAMAM G0, \(10^{-4}\) M PAMAM G0 are 126, 156, 168, and 208 mA/cm\(^2\), respectively. Compared with the data using 2.0 M methanol, the power densities of the un-doped and
Figure 4.13. Polarization curves for the MEA made from un-doped and doped Nafion® at 60 °C with 2 M aqueous methanol.
Figure 4.14. Polarization curves for the MEA made from un-doped and doped Nafion® at 60 °C with 5 M aqueous methanol.
doped membranes decrease accordingly due to more methanol crossover at higher methanol concentration.

Based on the experimental results, it can be found that the current density of the MEA made from $10^{-4}$ M PAMAM doped Nafion® at 0.4 V increased from 259 mA/cm$^2$ for 1 M methanol to 298 mA/cm$^2$ for 2 M methanol, then decreased to 208 mA/cm$^2$ for 5 M methanol. At low methanol concentration, the fuel cell performance goes up with the methanol concentration, and the optimum methanol concentration is 2 M in this case. However, since the methanol crossover rate is proportional to the methanol concentration to a great extent, it can also be found that the open circuit voltages decrease with increasing methanol concentration due to more serious methanol crossover that causes a larger mixed overpotential on the cathode.

4.4 Conclusions

The surface composition of Nafion® membranes doped with PAMAM G0 was characterized by XPS. The PAMAM G0 treatment has changed the transport properties of the Nafion® membrane. Direct TEM imaging of the Naifon® embedded with Ag nanoparticles demonstrated that PAMAM G0 can penetrate into the bulk of Naifon® through cluster channels to re-organize the distribution of sulfonate clusters by interacting with the sulfonic acid groups in different clusters. The presence of PAMAM G0 in the membrane causes the reduction of both of the proton conductivity and the methanol permeability, but an obvious increase in the selectivity when $10^{-4}$ M PAMAM
G0 was used. The power densities of MEAs made with Nafion® treated with $10^{-6}$ M PAMAM G0, $10^{-5}$ M PAMAM G0, or $10^{-4}$ M PAMAM G0 are higher than that of the undoped Nafion®, no matter at high concentration of methanol, 5 M, or low concentration of methanol, 1 M. Especially, when Nafion® was treated with $10^{-4}$ M PAMAM G0, the fuel cell performance is much improved. One can conclude that Nafion® treated with suitable concentration of PAMAM G0 will result in enhanced DMFC performance.
4.5 Reference


CHAPTER 5
CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The studies described in this dissertation mainly take advantage of the following three unique features of PAMAM dendrimers: 1) the interior amine and amide groups that can interact with ionic metal precursors through ligand exchange reactions; 2) the presence of an interior void space in the higher generation dendrimers; and 3) the exterior primary amine groups that permit further functionalization. The two applications of PAMAM dendrimers in fuel cells are summarized below.

5.1.1 Dendrimer Encapsulated Platinum Nanoparticles: Preparation, Characterization, and Applications in Fuel Cells

Among the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) is regarded as one of the most promising energy conversion devices. It is generally accepted that improving the utility of noble metal catalysts (typically Pt) and lowering their loading are vital to the success of PEMFC technology.

In an effort to improve the utility of Pt, this dissertation herein involves the use of amine-terminated PAMAM as both a template and a stabilizer to synthesize Pt nanoparticles by photoreduction and then self assembly of Pt DENs onto Nafion® to form a simplified MEA by electrostatic association. This approach produced electrocatalysts with reduced Pt loading and good dispersion. Furthermore, the
electrocatalysts are stabilized by encapsulation within the dendrimers. Therefore, the nanoparticles do not agglomerate, which maximizes and maintains the active area and improves catalyst efficiency. These nanoparticles exhibit a high specific activity for the oxygen reduction reaction and are inert to methanol oxidation at the same potentials, showing great potential for application in PEMFCs and DMFCs. This is a novel and potentially patentable result! A simplified MEA has been fabricated by the electrostatic self-assembly between Nafion® and Pt DENs. This MEA is stable due to a higher density of functional groups of PAMAM-NH$_2$ directly attached on the Nafion® surface. Two methods were proposed to increase Pt loading: layer-by-layer self assembly and immobilization of Pt DENs onto carbon paper. Approximately 80 layers are proposed to reach the required loading (ca. 0.2 mg/cm$^2$) using a dipping machine. Immobilization of Pt DENs and carbon powder simultaneously on a carbon fiber can be easily realized to enhance the Pt loading for fuel cells, which makes this a very promising method with which to replace the conventional method of electrode fabrication.

5.1.2 Modification of Nafion® with PAMAM G0 for Direct Methanol Fuel Cells

Direct methanol fuel cells (DMFCs) are promising power sources due to the simplicity of the system and the adaptability of methanol. One of the main impediments to the practical realization of the DMFC is the crossover of the methanol through the Nafion® membrane from the anode to the cathode.

In order to reduce the methanol crossover, this dissertation focuses on the modification of commercial Nafion® membranes by impregnating them with PAMAM G0 dendrimers. It was demonstrated that PAMAM G0 can penetrate into the bulk of Nafion® through cluster channels to re-organize the distribution of sulfonate clusters by
interacting with the sulfonic acid groups in different clusters. The presence of PAMAM G0 in the membrane causes reduction of both methanol permeability and proton conductivity, but a very beneficial trade off can be reached when a doping concentration of $10^{-4}$ M PAMAM G0 is used. The power densities of MEAs made with Nafion® treated with $10^{-6}$ M PAMAM G0, $10^{-5}$ M PAMAM G0, or $10^{-4}$ M PAMAM G0 are higher than that of the Nafion®. Especially, when Nafion® was treated with $10^{-4}$ M PAMAM G0, the fuel cell performance is much improved. One can conclude that Nafion® treated with a suitable concentration PAMAM G0 will enhance DMFC performance.

5.2 Future Work

5.2.1 Dendrimer Encapsulated Platinum Nanoparticles: Preparation, Characterization, and Applications in Fuel Cells

Although the Pt DENs show high specific catalytic activity for oxygen reduction reaction, the overpotential is still too high. One strategy to potentially overcome this problem would be to use a higher generation of PAMAM, so that more Pt nanoparticles can be formed within one dendrimer in order to improve electronic properties, as shown in Figure 5.1. Because conductance takes place based on an activated electron tunneling mechanism, electron conductivity depends highly on the interparticle distance.¹

Another problem is that the active surface area of the carbon fiber is too low. The surface area of carbon fiber is typically about $0.01 \text{ m}^2/\text{g}$, while the surface area of a carbon nanofiber can reach $2350 \text{ m}^2/\text{g}$.² Therefore, by using carbon nanofibers one can potentially reach the required Pt loading, even if only 4.5% of the carbon surface is covered by Pt nanoparticles.
By dipping the carbon paper into a dilute Nafion® solution, most of Pt DENs are expected to be in direct contact with the electrolyte, as shown in Figure 5.2, so proton transport loss can be minimized.

**Figure 5.1.** The strategy to reduce the overpotential.

**Figure 5.2.** The proposed structure of the interface.

### 5.2.2 Modification of Nafion® with PAMAM G0 for Direct Methanol Fuel Cells

Although the PAMAM doped Nafion® shows higher fuel cell performance, a number of issues still need to be addressed.

It is necessary to test if the stability of PAMAM doped Nafion® membranes is sufficient for the long operational lifetime required for commercial DMFCs. The existing
fuel cell test system needs to be modified to do longevity tests. Thereafter, Nafion® doped with $10^{-4}$ M PAMAM G0 should be selected for the first test. Polarization curves for the MEA would be recorded every 10 h, and analysis of the residual water from the cathode would be performed in an HPLC-MS system to test the stability of PAMAM-Nafion® combination.
5.3 References
