Experimental and theoretical study of cathode catalyst layer in PEM fuel cells

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**EXPERIMENTAL AND THEORETICAL STUDY
OF CATHODE CATALYST LAYER IN PEM
FUEL CELLS**

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Abstract

Fuel cells, which convert chemical energy directly into electrical energy with high energy conversion efficiency and low emissions, have been considered to be an option for power generation towards the hydrogen economy. For polymer electrolyte membrane fuel cell (PEMFC), proper water management is important to achieve high performance. On one hand, the Nafion electrolyte must be hydrated in order to maintain high proton conductivity. On the other hand, excessive water in cathode would cause electrode flooding, hindering the oxygen transport and blocking the electrochemical reaction sites. Due to the fact that the cathode catalyst layer is the location where oxygen reduction reaction happens and water produces, it is of particular important to systematically investigate the effects of the properties of cathode catalyst layer (CCL) on the water management and performance of PEM fuel cells.

The objectives of this study are to develop anti-flooding cathodes by optimizing the properties of the cathode catalyst layer (CCL), investigate the mechanisms of water transport within the cathode, and establish a mathematic model to analyze the water transport within the CCL of the PEM fuel cell. To fulfill these objectives, a novel anti-flooding CCL has been developed with the addition of oxygen permeable and hydrophobic dimethyl silicone oil (DSO) into the CCL to improve the water balance and oxygen transport within the cathode. Several characterization techniques, including mercury porosimetry, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), contact angle measurement, steady state polarization, transient current-step and electrochemical impedance spectroscopy, were

performed to understand the relationship between cell performance and CCL properties.

Fundamental understanding of water transport within the CCL could be obtained by conducting parametric study and guiding the design of high performance PEM fuel cells. The effect of DSO loadings in the CCL on the performance of the PEM fuel cells was investigated systematically. The results indicate that the loading of DSO in CCL plays a critical role in preventing the cathode from flooding and facilitating the oxygen transport under over-saturated conditions at both room temperature and elevated temperature. An optimal DSO loading in the CCL was found to be around 0.5 mg/cm^2 under the testing conditions in this work. The EIS measurements at different voltages also show that the DSO loaded CCLs are sensitive to the water content at low humidifying conditions and low current density.

The role of micro-porous layer (MPL) was found to be critical for the efficient water management in the PEM fuel cell. Since the pore size in the CCL is in the same order of magnitude as that in the MPL, the hydrophobic CCL modulated by DSO can function like a watershed as the MPL. The fuel cell with DSO loaded CCL without MPL has slightly poorer performance at low current density, but it prevails the fuel cell with normal CCL with MPL at high current density. Both of them can push the generated water back to the electrolyte so as to increase the proton conductivity in under-saturated condition. The cathode with both MPL and hydrophobic CCL has benefit at high humidified condition, but it suffers from high ohmic loss at low current density zone due to the poor water retention ability of the cathode. Hence, the

hydrophobic level of the CCL is critical and must be carefully controlled to balance the conflicting requirements of the electrolyte hydration and the cathode anti-flooding.

A mathematical model describing the major transport phenomena in cathode catalyst layer (CCL) of a PEMFC was developed. It reveals how the hydrophobicity of the CCL surface steers water, oxygen concentration and current density distributions in the CCL, thus affecting the performance of a PEMFC. The roles of wetting properties of the CCL on controlling the water transport for some operation conditions were simulated. This one-dimensional CCL model can help to fundamentally understand the water transport within the CCL and optimize the operating conditions and the CCL properties for improved fuel cell performance. In the light of the results achieved from the systematically experimental and modeling study, it is fundamentally clear that the optimized hydrophobicity of cathode catalyst layer is effective in expelling excessive water from the cathode, thus preventing the flooding and improving the fuel cell performance.

Chapter 1. Introduction

1.1 Fuel cells in general

Most of the world energy demands are associated with burning fossil fuels in low-efficiency thermal processes. Due to the depletion of fossil resources and increasingly stringent regulations imposed on environmental pollution throughout the world, alternative energy technologies have increasingly been caught attention in recent decades. Fuel cells, which convert chemical energy directly into electrical energy with high energy conversion efficiency and low emissions, have been considered to be an option for power generation in the 21st century towards the hydrogen economy. Their promising applications include transportation, distributed power generation and portable electronic devices due to their modularity and portability in nature.

According to the types of electrolyte materials used in a fuel cell, fuel cells can be classified into five most common types, namely polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). The direct comparisons of these five types of fuel cells are listed in Table 1.1 (Mathias *et al.* 2003). Among all fuel cell systems, polymer electrolyte membrane fuel cell (PEMFC) shows advantages in terms of portability, low operating temperature, potential for miniaturization, high power density, rapid start-up and good start-stop capabilities.

Type	Operating temp. (°C)	Anode reaction	Cathode reaction	Electrolyte	Advantages	Disadvantages
AFC	<100	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$	KOH	<ol style="list-style-type: none"> 1. Improved cathode performance 2. Potential for non-precious metal catalysts 3. Low materials costs, extremely low cost electrolyte 	<ol style="list-style-type: none"> 1. Must use pure H₂-O₂ 2. KOH electrolyte may need occasional replenishment 3. Must remove water from anode
PAFC	160-220	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	H ₃ PO ₄	<ol style="list-style-type: none"> 1. Mature technology 2. Excellent reliability and long-term performance 3. Electrolyte is relatively low-cost 	<ol style="list-style-type: none"> 1. Expensive platinum catalyst 2. Susceptible to CO and S poisoning 3. Electrolyte is a corrosive liquid that must be replenished during operation
MCFC	600-800	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$1/2\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$	Molten Li ₂ CO ₃ +K ₂ CO ₃	<ol style="list-style-type: none"> 1. Fuel flexibility 2. Non-precious metal catalyst 3. High-quality waste heat for cogeneration applications 	<ol style="list-style-type: none"> 1. Must implement CO₂ recycling 2. Corrosive, molten electrolyte 3. Degradation and lifetime issues 4. Relatively expensive materials
SOFC	800-1000	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$	$1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$	2 ZrO ₂ +Y ₂ O ₃	<ol style="list-style-type: none"> 1. Fuel flexibility 	<ol style="list-style-type: none"> 1. Significant high-

	500-600				2. Non-precious metal catalyst 3. High quality waste heat for cogeneration applications 4. Solid electrolyte 5. Relatively high power density	temperature materials issues 2. Sealing issues 3. Relatively expensive components and fabrication
PEMFC	~80	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	Proton exchange membrane	1. Highest power density of all the fuel cell classes 2. Good start-stop capabilities 3. Low-temperature operation makes it suitable for portable application	1. Expensive platinum catalyst 2. polymer membrane and ancillary components are expensive 3. active water management is often required 4. Very poor CO and S tolerance

Table 1.1 Major types of fuel cells classified by the electrolyte used

1.2 Principle of PEM fuel cell

The basic structure of a PEM fuel cell consists of an electrolyte membrane sandwiched by a porous anode and a porous cathode together with two flow field plates providing the support and transporting the reactants/products. A schematic diagram of a PEM fuel cell is shown in Fig. 1.1. The sandwich structure of porous anode/membrane/porous cathode is referred as membrane electrode assembly (MEA), which is the heart of a fuel cell system. The porous electrode, typically named the gas diffusion electrode (GDE), is composed of a thin catalyst layer and a backing layer. The thin catalyst layer is the site for the electrochemical reactions. While, the porous backing layer, also called as gas diffusion layer (GDL), transports the reactant/product between the reaction sites and the gas flow channel. At the anode, hydrogen is oxidized to release electrons and protons as follows:

Fig. 1.1 Schematic of a PEMFC with reactant/product and proton flow path

The electrons travel through the external circuit to form the current. The protons transport through the polymer electrolyte membrane from the anode side to the

cathode side, react with oxygen and combine with two electrons to form water molecule as follows:

Thus, the overall fuel cell reaction is

The maximum electrical power, $W_{\max}$, obtained in fuel cell operation at constant temperature and pressure process is given by the change in Gibbs free energy, ΔG , of the electrochemical reaction:

$$W_{\max} = \Delta G = -nFE \quad (1.4)$$

Where n is the number of electrons participating in the reaction, F is Faraday's constant (96485 coulombs/mol), and E is the theoretical equilibrium potential of the cell. For reactants and products in their standard states conditions (298 K and 1 atm), represented by the superscript “°”, the theoretical equilibrium potential of the hydrogen/oxygen fuel cell can be calculated as follows:

$$E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{237340 \text{ (J mol}^{-1}\text{)}}{2 \times 96485 \text{ (C mol}^{-1}\text{)}} = 1.23 \text{ V} \quad (1.5)$$

1.3 Performance of a fuel cell

A typical polarization curve to characterize fuel cell performance is illustrated in Fig. 1.2. The theoretical equilibrium potential under operating conditions can be calculated from:

$$E = E^\circ + \frac{RT}{2F} \ln \left[\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right] + \frac{RT}{2F} \ln [p_{\text{O}_2}]^{\frac{1}{2}} \quad (1.6)$$

Practically, the open circuit potential is always slightly lower than the theoretical potential. In most cases, this is due to small amount of hydrogen crosses through the electrolyte membrane, causing mixed potential at the cathode side. Hydrogen crossover is a function of membrane permeability, membrane thickness, operating conditions and hydrogen partial pressure. For some extreme cases, a very low open circuit voltage may indicate either hydrogen leak or electrical short circuit.

Fig. 1.2 Schematic diagram of a fuel cell polarization curve

As indicated in Fig. 1.2, the polarization loss of the fuel cell during operation is mainly composed of three parts, namely activation overpotential, ohmic overpotential, and concentration overpotential. The activation overpotential, η_{act} , which arises from the kinetics of charge transfer reactions across interfaces and represents the magnitude of activation energies, is mainly associated with the sluggish oxygen reduction kinetics and is dominant at low current density, which can be expressed by Butler-Volmer equation as follows:

$$i = i_o \left\{ \exp \left[\frac{\alpha z F \eta_{act}}{RT} \right] - \exp \left[\frac{-(1-\alpha) z F \eta_{act}}{RT} \right] \right\} \quad (1.7)$$

where R is the universal gas constant, T the temperature, α the electron transfer coefficient of the reaction, i the current density, and i_o the exchange current density. The exchange current density of the anode is several orders of magnitudes larger than that of the cathode. Thus, the anode activation overpotential is much lower than the cathode activation overpotential.

The ohmic overpotential, η_{ohmic} , which obeys Ohm's law, includes the electronic, ionic and contact resistance of fuel cell components:

$$\eta_{ohmic} = i R_{ohmic} \quad (1.8)$$

Because ionic charge transport tends to be more difficult than electronic charge transport, the ionic resistance is the main contributor to the total R_{ohmic} (O'Hayre *et al.* 2002). The ohmic loss dominates the fuel cell performance in the mid current density range of the polarization curve, which is dependent on the cell geometry, the materials used and the operating temperature.

As reactants are consumed by the electrochemical reaction, the mass transport becomes the dominant limitation under high current density, leading to the occurrence of the limiting current. During fuel cell operation, water is produced in the cathode. If the water cannot be promptly removed from the cathode, flooding will happen in the cathode, hindering the oxygen transport and increasing the concentration overpotential dramatically.

1.4 The challenges and water management in a PEM fuel cell

The oxygen reduction reaction (ORR) that takes place in the cathode is critical to determine the performance of a PEM fuel cell. The ORR kinetics is much more sluggish than the hydrogen oxidation reaction (HOR). Furthermore, the diffusivity of oxygen is several times lower than that of hydrogen, causing more significant concentration polarization at the cathode under high current density. Extensive efforts have been put in two ways to improve the cathode performance. One way is to develop novel electrocatalysts so as to improve the sluggish ORR kinetics and reduce the activation polarization. Another way is to optimize cathode structure so as to facilitate the transport of oxygen within the cathode and alleviate the water flooding, thus significantly lowering the concentration polarization and improving the performance of PEM fuel cell.

Fig. 1.3 Schematic of water transport inside a PEM fuel cell

Figure 1.3 schematically illustrates the water transport in a PEM fuel cell. Water is introduced into the fuel cell system by the humidified reactant gases and the electrochemical reactions at the cathode side. It not only transports from the cathode catalyst layer to the gas flow channel through the gas diffusion layer by evaporation,

water-vapor diffusion and capillary transport, but also tends to migrate through the membrane via the combined effects of the electro-osmotic drag and back diffusion. Due to the co-existence of gas and liquid phases, the two-phase flow and transport are the main problems for the cathode optimization. Under some operation conditions, especially at high current density, low temperatures, and high humidification levels, there is an excessive amount of water accumulated in the cathode, causing serious “flooding” phenomenon. Oxygen starvation can lead to current reversal in a PEM fuel cell stack where the oxygen reduction reaction (ORR) would be replaced by the proton reduction reaction (PRR).

Under such extreme condition, the output of a PEM fuel cell stack will be seriously impaired. Additionally, excessive liquid water can also lead to non-homogeneous current density, ineffective heat removal and membrane swelling (Li *et al.* 2008), resulting the delamination of fuel cell components during the thermal cycling associated with freeze/thaw processes (Kim *et al.* 2008).

1.5 Objectives of the research project

Water management has a significant impact on the overall performance of the fuel cell system. On the one hand, the polymer membrane in PEM fuel cells, typically Nafion, must be hydrated in order to maintain high proton conductivity. On the other hand, excessive water in cathode would cause electrode flooding, hindering the oxygen transport and blocking the electrochemical reaction sites. Thus, water should be carefully balanced in PEM fuel cell to meet the conflicting requirements of electrolyte hydration and electrode anti-flooding. Intensive research activities have focused on

investigating the effects of GDL and flow field design on water management. However, little attention has been paid to experimentally explore the role of the cathode catalyst layer on water management. Due to the fact that the cathode catalyst layer is the location where water produces, it is worthwhile to systematically investigate the effect of the properties of cathode catalyst layer on water management and performance of PEM fuel cells.

The objectives of this study are to (i) develop anti-flooding cathodes by optimizing the properties of the cathode catalyst layer (CCL); (ii) investigate the mechanisms of water transport within the cathode; and (iii) establish a mathematic model to analyze the water transport within the CCL of the PEM fuel cell. Fundamental understanding of water transport within the CCL can be obtained by conducting parametric study and guiding the design of high performance PEM fuel cells.

1.6 Scope of the research project

The main scope of the research project is outlined below:

- a. Characterization of PEM fuel cells with different CCLs, in particular
 - using scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) to study the microstructure of different CCLs'
 - measuring contact angle to determine the surface hydrophobicity of different CCLs
 - using porosimeter to investigate the pore distributions of different CCLs
 - using electrochemical impedance spectroscopy to understand the flooding mechanism.

- b. Development of anti-flooding cathode by optimizing the CCL with hydrophobic dimethyl silicone oil (DSO), in particular
 - Effect of DSO loading on water management and the fuel cell performance
 - Effect of operating condition on the water management in PEM fuel cell
 - Application of the in-house developed anti-flooding cathodes in high performance air-breathing fuel cell stack.

- c. Comparisons of water management and performance of the PEM fuel cells with different CCLs in various cathode structures
 - Development and performance evaluation of a normal CCL on top of a GDL with micro porous layer
 - Development and performance evaluation of a DSO loaded CCL on top of a GDL with micro porous layer
 - Comparisons of different CCLs on GDL with and without micro porous layer to evaluate the water control strategy.

- d. Development of a mathematical model to fundamentally understand water transport within the CCL and its effect on the fuel cell performance, which includes
 - Validation of the mathematic model with experimental data
 - Effect of operating condition on the water saturation within the CCL
 - Effect of hydrophobicity of the CCL on the fuel cell performance
 - Effect of CCL microstructure on the fuel cell performance

Chapter 2. Literature review

2.1 Electrochemical Reaction in PEM fuel cell cathode (ORR)

In PEM fuel cells, the most common oxidant in the cathode is oxygen which can be a pure oxygen gas from a tank or oxygen directly from air. Oxygen reduction reaction (ORR) happens with continuous production of water at the three phase boundary among the electrocatalyst, the ionic conductor and gas phase:

It has been widely accepted that the ORR can occur by two different reaction pathways, namely the direct four-electron pathway and the peroxide pathway. Antoine and Durand (Antoine and Durand 2000) confirmed that a direct four-electron transfer is the main ORR mechanism on platinum nanoparticles in PEM fuel cells in a study using a rotating ring disk electrode (RRDE). In acidic media, the Damjanovic mechanism has been widely accepted under steady state conditions on bulk platinum (Damjanovic and Brusic 1967; Antoine *et al.* 2001), in which the first electrochemical step was assumed to be the protonation of the O_2 molecule on platinum surface with a very low partial coverage of adsorbed oxygen. This step was considered to be the rate determining step (rds) for ORR:

Thus, the reaction is first order with respect to O_2 pressure in the whole range of potentials. A new mechanism in accord with Damjanovic's statement was proposed that the adsorbed $\text{O}_2\text{H}_{\text{ads}}$ undergoes a chemical step and a subsequent electrochemical reaction to form water molecule as follows (Diard *et al.* 1993):

Antoine *et al.* used electrochemical impedance spectroscopy (EIS) and RRDE technology to confirm the presence of two electrochemical steps in the ORR mechanism. They concluded that the mechanism for oxygen reduction proposed by Damjanovic and coworkers on bulk platinum in acidic medium was also valid for Pt nanoparticles (Antoine *et al.* 2001).

2.2 Water transport and liquid water visualization in the PEM fuel cell

Over the past few years, the importance of water management for the successful operation of PEM fuel cell has stimulated intensive researches to study the liquid water transport in the PEM fuel cell. As shown in Fig. 2.1 (a), the slopes of the polarization curves of the PEM fuel cell become much steeper at higher current density because of the flooding. This significant performance loss is attributed to the greatly reduced oxygen transport rate incurred by water flooding at high current densities where the water generation rate exceeds the water removal rate. In the stability test, the time-dependent fluctuations of cell voltage also typically imply the flooding phenomenon (Fig. 2.1 (b)). When water retains in the cathode to some extent, the gas flow path will be temporarily blocked or the catalyst surface covered by water droplet will be inaccessible to the incoming oxidant gas. As a result, the cell voltage drops off immediately at fixed current density. However, the blocking of the flow gas induces a sudden build-up of local pressure that may quickly flushes out the excess

liquid water. This is why the cell voltage can be restored periodically. The periodic build-up and removal of liquid water in the cell causes the inconsistent and unstable fluctuation in the cell performance.

Fig. 2.1 (a) typical polarization curves of a PEM fuel cell illustrating the effect of water flooding on cell performance, (b) water flooding pattern in a PEM fuel cell operated at constant current density (Li *et al.* 2008)

Besides the cell voltage losses, water flooding can also be indicated by some changes in the characteristic properties of a PEMFC which involves (i) the pressure drop between the inlet and outlet of the fuel cell when electrode or flow field is blocked by the liquid water, (ii) the resistance alteration of the cell when flooding or dry membrane happened (Barbir *et al.* 2005), and (iii) uneven local distribution of current density and temperature because of different distribution of liquid water in the electrode (Hakenjos *et al.* 2004). In addition, electrochemical impedance spectra of a fuel cell at different voltages were also employed to detect the failure operation associated with flooding and membrane drying (Le Canut *et al.* 2006).

Other than the physical and performance indication of the flooding phenomenon in PEM fuel cell, liquid water visualization is another popular method to investigate the

water transport in the PEM fuel cell during operation. There are several imaging techniques including direct optical visualization (Tüber *et al.* 2003; Hakenjos *et al.* 2004; Yang *et al.* 2004; Zhang *et al.* 2006; Spornjak *et al.* 2007), neutron imaging (Satija *et al.* 2004), X-ray radiography (Sinha *et al.* 2006), electron microscopy (Nam and Kaviany 2003) and magnetic resonance imaging (Tsushima *et al.* 2004). Among them, neutron imaging is the only diagnostic tool that has the advantages of in situ applicability, minimal invasiveness and the ability to provide local information (Stumper *et al.* 2005). With the sensitivity to hydrogen containing compounds and insensitivity to common fuel cell materials, neutron imaging is always employed to quantify the liquid water distribution in the PEM fuel cell during operation. However, it has limited application due to the availability of necessary neutron sources.

Fig. 2.2 Two consecutive environmental scanning electron micrographs (ESEM) of a diffusion medium exposed to water-vapour saturated atmosphere. (Nam and Kaviany 2003)

Nam and Kaviany (2003) employed an environmental scanning electro-microscope (ESEM) to visualize condensed water droplet on GDL in ex situ with a saturated water atmosphere at low temperature and vapor pressure. They found that micro-droplets transport near the catalyst layer and then agglomerate with other liquid bodies to form macro-droplets as shown in Fig. 2.2. They built a one-dimensional water saturation

model for GDL based on consecutive ESEM images of water droplet growth as seen in Fig. 2.3. Gurau *et al.* (2006) employed SEM to visualize the water droplet formed on a Toray GDL and concluded that the internal contact angle measurement is necessary to estimate the transport properties inside the GDL pores. However, due to the complex structure of the GDL material, the direct method for estimating the internal contact angle using goniometry on micrographs is impractical.

Fig. 2.3 water transport model cited from (Nam and Kaviani 2003)

Recently, optical photography has been used extensively to directly visualize the water transport in a transparent PEM fuel cell under various operating conditions. Yang *et al.* (2004) revealed that water droplets emerged intermittently on preferential locations on the GDL surface and grew to a size comparable to the channel size under the influence of surface adhesion. They concluded that the coalescence of water droplets and their migration along the hydrophilic surfaces of the gas channel were the main mechanisms of the liquid water removal. Similar method was used by Tübe *et al.* (2003). Their results clarified the necessity of the proper control of water content inside an operating fuel cell such as air-flow regulation and air humidity control at low temperature. The characteristics of the GDL take important role in the water control. At low temperature around 30°C, the hydrophilic carbon paper presented better

performance than hydrophobic carbon paper because the hydrophilic coating in the backing layer prevented total clogging of air channels. Through observing the water transport in a transparent single-serpentine PEM fuel cell, Spornjak *et al.* (2007) found that the micro porous layer (MPL) in the cathode side created a pressure barrier to increase the water back diffusion from cathode and anode.

Due to the opaque nature of traditional GDL, most of the direct visualization tools mainly focus on liquid water on the surface of the GDL and along the flow channel. Zhang *et al.* (2007) reported the visual characterization of the cathode catalyst layer (CCL) with the help of the microvisualization system and identified the importance of the CCL in water control. They indicated that it was a distinguishing ability of the CCL to remove water by evaporation. Reducing the pore size and increasing hydrophobic property preferentially retains water in the gas phase and alleviates flooding within the CCL. For efficient catalyst utilisation, the CCL should have optimal distribution of hydrophobic and hydrophilic pore, so that there is a balance between the gaseous transport of reactants and the water retention to facilitate the ionic conductivity. Nam *et al.* (2009) also showed some ESEM pictures on water breakthrough in CCL and implied that water droplets could grow from small to very large droplets so as to deteriorate the cell performance.

2.3 Effects of PEM Fuel cell structure on the water management

The gas diffusion electrode (GDE) in a PEM fuel cell is a key component that affects the performance and cost of the fuel cell due to the content of noble metal Pt in its

catalyst layer. Typically, a GDE in a PEM fuel cell structurally comprises a catalyst layer (CL) and a gas diffusion layer (GDL). There are two classes of strategies to mitigate flooding issues of the PEM fuel cell (Li *et al.* 2008). The first is based on system design and engineering such as active pump integration (Litster *et al.* 2009), reactant humidity controlling, flow rate controlling, temperature and pressure controlling (Park and Caton 2008), which are often accompanied by significant parasitic power loss. The second class is based on MEA design and engineering which involves modifying the material and structural properties of the CCL, GDL, membrane and bipolar plate surface condition to function in the presence of liquid water. The designs of the fuel cell structure have great effects on the water control during the operation of a PEM fuel cell, especially at room temperature.

2.3.1 Catalyst layer

The catalyst layer is in direct contact with the membrane and the gas diffusion layer. It mainly consists of electrically connected catalyst particles, ionomer and pore space for reactant gases to transport; each of which is critical for the formation of the triple phase boundaries where the ORR or HOR takes place. It is well known that platinum and platinum-containing catalysts are the most effective catalyst materials in terms of both activity and stability. Research efforts on PEM fuel cell catalysts layer have been focused on reducing costly platinum loading. In addition to catalyst loading, there are a number of catalyst layer properties that have to be carefully optimized to achieve high utilisation of the catalyst materials. For example, gas diffusion, ionic and electrical conductivity, and the level of hydrophobicity of a CCL should be delicately balanced. The role of the catalyst layer in water balance has never been explored in

depth either experimentally or theoretically, in contrast to the intensive research activities studying the effects of the GDL and flow field on water management (Zhang and Shi 2006; Li *et al.* 2008). However, water balance in the CL is critical for the long-term performance and durability of PEM fuel cells. An insufficient amount of water in the CL would result in reduced ionic conductivity and make the catalyst surface partially accessible, which will, in turn, contribute to resistive and kinetic cell voltage loss (Stumper *et al.* 2005). Too much water, on the other hand, will block the catalyst surface to decrease the reactive surface area and constrain reactant gas transport which results in significant mass transport performance degradation.

The first generation of the PEM fuel cell that used PTFE-bound Pt black electrocatalysts with 4 mg/cm² Pt loading as electrodes exhibited excellent long-term performance (Wilson *et al.* 1995). However, the high cost of the electrodes prevented this method from commercialization. With the development of the nanotechnology, a generous amount of efforts have been directed at reducing Pt loading below 0.4 mg/cm² by using PTFE-bound carbon-supported nano-size Pt electrocatalysts and Nafion impregnated method. To increase the utilisation of the catalyst, Nafion was gradually incorporated into the catalyst ink to bind with the catalyst and increase the proton conductivity in the catalyst layer. Currently, the most commonly used method for fabricating the CL is the hydrophilic method (Nafion-bound method), which was also called as thin film method.

(1) PTFE-bound methods

The PTFE-bound catalyst layer was referred as the hydrophobic catalyst layer, in which PTFE is employed to bind the catalyst particles. It was first developed by

Neidrach and Alford in 1969 (1969) in Gemini missions. The conventional catalyst layers are generally featured by high platinum loading of 4 mg/cm^2 when Pt black or Pt supported on carbon are employed. Until recent decades, this method was able to reduce the platinum loading of previous PEM fuel cells by a factor of 10, from 4 mg/cm^2 to 0.4 mg/cm^2 . Some of the original PEM fuel cells with low platinum loading featuring PTFE-bound catalyst layers were fabricated by Ticianelli *et al* (1988). The advantage of this method is that PTFE can be incorporated into the catalyst layer before the application of Nafion, so that the ultimate electrode will have a controllable hydrophobicity to reduce the possibility of getting serious flooding, which is sometimes very important for water control and mass transport in the cathode of PEMFC.

It is worthwhile to note that only catalyst in contact with both electrolyte material and reaction gas is electrochemically active. In order to provide ionic transport to the catalyst sites thereby extending the three dimensional reaction zones, Nafion was impregnated into the electrocatalyst layer by brushing or spraying. The impregnated electrodes were then hot pressed onto the both side of the membrane to ensure good ionic conduction across the interface. Nafion impregnation was critical in improving the utilisation of the catalyst and the performance of PEM fuel cell. Uchida *et al.* (1995) studied the effects of Nafion and PTFE in the catalyst layer on the performance of a PEM fuel cell. They concluded that the optimum content of Nafion in the PTFE loaded carbon electrode was 1.0 mg/cm^2 . Both Nafion and PTFE were able to affect the size of the large pore with diameter of ca. $0.04 \text{ }\mu\text{m}$, where was the only location that both Nafion and PTFE co-existed as shown in Fig. 2.4. The ratio of PTFE to carbon of the electrodes principally influenced fuel cell performance at high

current density. The optimum ratio of the PTFE to carbon at 1200 mA/cm^2 was 50. This explained that the hydrophobic PTFE-C worked to supply reactant gas to the reaction site in the secondary pores covered by Nafion and to exhaust the product water from there.

Fig. 2.4 Schematic internal structure of the catalyst layer (Uchida *et al.* 1995)

Lee *et al.* (1998) investigated the effects of Nafion impregnation on commercial low platinum-loading PEM electrodes in terms of performance using H_2/O_2 and H_2/air as reactant gased. Nafion was impregnated into electrodes by a brushing method with the Nafion loading varying from 0 to 2.7 mg/cm^2 . Correlation of Nafion loading with the activation polarization characteristics showed a non-linear relationship. When air is used as an oxidant, an initial increase in performance is seen for a loading up to 0.6 mg/cm^2 . For H_2/O_2 system, the optimal loading of Nafion is 1.9 mg/cm^2 . Their results indicated that the diffusional resistance due to increased Nafion thin film thickness and high penetration of the Nafion into the catalyst layer were the main contributors to the mass transport. Without the addition of some Nafion, the most of the catalyst sites were inactive due to the lack of the three-phase boundary. Similar works have been done by Ticianelli *et al.* (1988). They brushed different amount of

Nafion onto the 0.35 mg/cm² Pt loading gas diffusion electrode and found that an optimum Nafion content in the electrode is necessary to minimize ohmic and mass transport overpotentials. As explained in Fig. 2.5, the extension of three dimensional reaction zones with Nafion impregnation of the electrode was been confirmed by cyclic voltammetry. However, when too much Nafion is used, it covers some of the platinum site which incurs mass transport problem. Researchers have been continuing to develop new strategies for Nafion impregnation. Cheng *et al.* (1999) claimed that if the PTFE-bound electrode was immersed in a diluted Nafion solution and treated ultrasonically, the utilisation of Pt electrocatalyst has achieved 78%, in contrast with only 22% for electrode Nafion-impregnated by brushing.

PTFE can increase the diffusivity of gases and further provide hydrophobicity to an open pore to avoid being blocked up with water, which is desirable for the gas-diffusion portion. Although this property is desirable, a performance penalty is paid for decreasing the humidity of Nafion and blocking the proton or electron passageway in parts of the catalyst layer, leading to insufficient utilisation of the catalyst. Perez *et al.* (Perez *et al.* 1998) used a PTFE incorporated Pt/C electrode on graphite substrate. The low surface values obtained by CV in their experiment can be explained by the low catalyst utilisation due to the presence of PTFE in the electrode. Furthermore, it is very difficult to control the amount of Nafion applied and is impossible to have homogeneous distribution of Nafion in the entire catalyst layer, which results in a catalyst utilisation of only about 10-20%. Too much Nafion will also incur mass transport problem. Therefore, the utilisation of catalyst and the cell performance are strongly dependent on how the Nafion is incorporated and its distribution in the catalyst layer (Passalacqua *et al.* 2001). In addition, this kind of electrodes is prone to

delaminate from the membrane, especially when the stack is shut down and then turned on again. Even though PTFE features effective binding qualities and imparts beneficial hydrophobicity in the gas diffusion layers, there is no particular benefit to its presence in the catalyst layer (Wilson and Gottesfeld 1992). The well-known Nafion-bound catalyst layer eventually replaces the PTFE-bound one and become the dominant catalyst layer fabrication method.

Fig. 2.5 (A) Cyclic Voltammograms for Nafion-impregnated cathodes (0.35 mg Pt/cm^2) in argon atmosphere: black line, 10% Nafion; grey line, 3.3% Nafion; (B) Cell potential current density plots for H_2/air , fuel cells with these cathodes and similar anodes. black line, 10% Nafion; grey line, 3.3% Nafion (Ticianelli *et al.* 1988)

(2) Thin film methods (Nafion-bound)

The thin film catalyst layer is directly casted onto the GDL from a solubilized ionomer/suspended catalyst solution to form a thin film that relies upon the Nafion as both the binder and the ionic conductor. Since invented in 1992, the thin film

electrode is becoming the most common used electrode design. The first thin-film catalyst layer was developed by using a transfer printing method, i.e. casting CL onto Teflon blanks, hot-pressing the formed CL onto the membrane, and then peeling off the Teflon blanks as shown in Fig. 2.6. Alternatively, the catalyst layer can be casted onto the membrane using the direct coating method. According to the results of Wilson and Gottesfeld (1992), the direct coating method not only simplified the fabrication process but also improved the interfacial continuity between the ionomer in the membrane and the ionomer in the catalyst layer, which resulted in more robust CL. Consequently, the fuel cells fabricated using this method with ultra-low Pt loading, such as 0.12 mg/cm^2 , showed performance superior to those fabricated with other approaches. Chun *et al.* (1998) further enhanced the direct coating of thin film CL to achieve the intimate interface between the Nafion in the catalyst ink and the Nafion membrane. To avoid chemical transformation of Nafion, Gamburzev and Appleby (2002) painted or printed electrocatalyst–Nafion ink onto a GDL to produce the CL. After treatment with some pore-former, the performance of the fuel cell with this type of MEA achieved 340 mA/cm^2 at 0.7V .

The thin film catalyst layers are superior to the PTFE bound catalyst layers in terms of the performance and the catalyst utilisation, which can achieve a power density at almost twice of the PTFE-bound catalyst layers (Litster and McLean 2004). Cheng *et al.* (1999) directly compared the utilisation of the platinum and the morphology of the PTFE-bound and the Nafion-bound thin film catalyst layers. They concluded that the catalyst utilisation increased from 22% for the PTFE bound CL impregnated with Nafion by brushing method to 45.4% for the Nafion-bound thin film CL. They explained that the drop of platinum utilisation may mainly attribute to the blocking

effect of the Nafion solid on the catalyst surface due to the coverage of Nafion layer or clumps on many carbon particles or agglomerate. Chun *et al.* (1998) also compared the performance of the PEM fuel cells with the PTFE-bound CL and the Nafion-bound CL. It is obvious to see that the fuel cells with the Nafion-bound CL have much better performance than that with the PTFE-bound CL.

Fig. 2.6 Primary steps in the fabrication of a thin film catalyst layer bonded to an ionomeric membrane through a transfer printing method (Wilson and Gottesfeld 1992)

The electrode performance is essentially determined by the combined effects of the ionic conductivity, electronic conductivity and mass transport through the electrode. The parameters that can affect the above properties have been intensively investigated to improve the performance of the PEM fuel cell, e.g. loading of platinum, content of Nafion, solvents used to disperse the catalyst particles, and other unusual materials to change the structure of CL such as pore former, thermoplastic ionomer, silica and dimethyl silicon oil.

Table 2.1 Comparison of the performance of the fuel cells with various MEAs (Nafion 115 membrane, H₂/O₂ pressure =1:1 atm, at 90 °C, flow rate: H₂=8.5 l/min, O₂=3.8 l/min) (Chun *et al.* 1998)

Type of electrode	Power density	Power density
	at 200 mA/cm ²	at 0.6V
	(mW/cm ²)	(mW/cm ²)
PTFE-bound	114	93
Thin film, direct membrane coating	145	200
Thin film, transfer printing (20 % Pt/C)	129	147
Thin film, transfer printing (40 % Pt/C)	123	132

(a) Loading of Platinum

It is well-known that O₂ kinetics and O₂ diffusion at the cathode are the two primary limitations for the PEM fuel cell performance. To increase the reaction sites, the common method is to increase the Pt loading so as to enhance the O₂ reduction reaction. The first generation of PEM fuel cells featured expensive Pt loading of 4-10 mg/cm² using PTFE-bound CL with Pt-black as the electrocatalyst (Wilson and Gottesfeld 1992). Later, by substituting the Pt-black with carbon supported catalyst of higher surface area, the Pt loading had been significantly reduced to 0.4 mg/cm² (Ticianelli *et al.* 1988). With the increased utilisation of Pt catalyst, the MEAs fabricated by thin film method demonstrated high performance with low Pt-loadings of around 0.2 mg/cm² (Wilson *et al.* 1995). Paganin *et al.* (1996) also confirmed that the Pt loading can be reduced to 0.2 mg/cm² in a cathode without affecting the fuel cell performance. Gasteiger *et al.* (2004) reduced the Pt loading from 0.4 to 0.05 mg/cm² at anode and from 0.4 to 0.2 mg/cm² at cathode and studied the effect of the

Pt loading reductions on the fuel cell performance. They found that there was no significant voltage loss for anode Pt loading reduced to 0.05 mg/cm^2 . However, the cell voltage lost 10-20 mV due to the reduction of the cathode catalyst loading from 0.4 to 0.2 mg/cm^2 , which was consistent with the kinetic losses of oxygen reduction reaction.

Currently, there are some emerging methods reported to improve the catalyst utilisation so as to reduce the Pt loading less than 0.1 mg/cm^2 , such as electrodeposition (Kim *et al.* 2004; Wei *et al.* 2005), sputtering deposition (O'Hayre *et al.* 2002; Gruber *et al.* 2005; Gasda *et al.* 2009; Tang *et al.* 2009), dual ion-beam assisted deposition (Saha *et al.* 2006), electro-spray method (Benitez *et al.* 2005), and electroless deposition (Sasaki *et al.* 2004; Travitsky *et al.* 2006; Beard *et al.* 2007). Among the methods, the electrodeposition method exhibited the highest Pt utilisation and the best performance because the Pt was deposited only onto the active zones. The sputtering method can achieve relatively low Pt loading, which is the most promising technology for micro-systems and automotive application (Wee *et al.* 2007). However, one should note that the performance of the fuel cells with cathodes deposited with sputtering method can vary significantly depending on the thickness of the catalyst layer.

(b) Catalyst supports

For decades, carbon black such as Vulcan XC-72 has been the most widely used electrocatalyst support. Until recently, many nanostructured carbon materials such as nanotubes (Li *et al.* 2006), nanofibre (Bessel *et al.* 2001), and nanoporous hollow sphere (Yu *et al.* 2002) have been chosen as catalyst supports to achieve low Pt

loading. Because catalysis is a surface process, high surface area of the catalyst is required to reduce the catalyst loading. In comparison with the most widely used Vulcan XC-72R carbon black support with electronic conductivity of 4.0 S cm^{-1} and specific surface area of $237 \text{ m}^2\text{g}^{-1}$, CNTs have higher electronic conductivity of 104 S cm^{-1} and extremely larger specific surface area of $200\text{-}900 \text{ m}^2\text{g}^{-1}$. Moreover, CNTs have also been shown to be more corrosion resistance than carbon black under simulated fuel cell operation conditions, offering great potential as catalyst supports (Rajesh *et al.* 2000; Tian *et al.* 2006). The morphology and catalytic activity of the catalysts supported on the CNTs are strongly dependent on their synthesis methods and conditions. Many preparation methods, such as impregnation method, microwave assisted process, electrodeposition, sputtering deposition technique, self-regulated reduction of surfactants, and so on, have been explored to synthesize highly-dispersed CNT-supported catalysts. Table 2-2 shows the representative synthesis methods for the CNT-supported catalysts.

Table 2.2 Representative synthesis methods for the CNT-supported catalysts

Preparation method	catalyst	Agents	Particle size, nm	Reference
impregnation method	Pt/MWCNT	H_2PtCl_6 +ethylene glycol	2-4	(Li <i>et al.</i> 2006)
microwave assisted process	Pt/MWCNT	H_2PtCl_6 +ethylene glycol	3	(Tian <i>et al.</i> 2006)
Electrodeposition	Pt/SWCNT	H_2PtCl_6 solution	20	(Wei <i>et al.</i> 2005)
sputtering deposition technique	Pt/CNT array	Pt	2	(Sun <i>et al.</i> 2005)
self-regulated reduction of surfactants	Pt/CNT	SDS+ H_2PtCl_6 solution	1.6-1.8	(Lee <i>et al.</i> 2005)

(c) Content of Nafion

Nafion is another essential material in the catalyst layer, which is used both as a proton conductor and a binder in the electrode with relatively low Pt loading. There exists an optimal content of Nafion in achieving a compromise between the Pt utilisation and mass transport. When the Nafion content is low, the electrocatalyst in contact with Nafion is poor and it cannot provide sufficient proton conductivity. As a result, the active area is low and thus the low catalyst utilisation. On the other hand, if too much Nafion is used in the catalyst layer, the excess Nafion would cover the catalyst surface and hinders the gas transport. Furthermore, the more the hydrophilic Nafion in the catalyst layer, the more water will be trapped in the catalyst layer which may induce the flooding phenomena. Passalacqua *et al.* (2001) illustrated the role of Nafion in the catalyst layer in Fig. 2.7, which suggested that the amount of Nafion should be meticulously controlled. The results from Paganin *et al.* (1996) showed that the fuel cell performance increased with increasing the Nafion loading from 0.87 mg/cm² (17% of catalyst layer weight) to 1.75 mg/cm² (30% of catalyst layer weight) in the thin film catalyst layer. However, when the Nafion loading is beyond 2.2 mg/cm², the fuel cell performance deteriorated at higher current densities. Similar results also reported by other researchers (Antolini *et al.* 1999; Li and Pickup 2003; Ma *et al.* 2009). Li and Pickup (2003) also found that too much Nafion in the CL would not increase the ohmic resistance but it increases the oxygen transport resistance seriously. While at low Nafion loading, the electronic resistance is much higher than that of 30% Nafion loading, indicating that Nafion plays a significant role as a binder. Recently, Ma and co-worker (2009) examined the surface morphology of electrodes with different contents of Nafion by atomic force microscopy (AFM) and electrostatic force microscopy (EFM). They observed that the enlarged grain, reduced

pore size and decreased surface roughness with the increase of the ionomer contents in the catalyst layer. For a practical use, the optimal Nafion loading can be calculated by using some empirical equations obtained from the experimental data and the literature (Antolini *et al.* 1999):

$$\text{Loading of Nafion} \approx 56 L_{\text{Pt}} / P_{\text{Pt}} \quad (2-5)$$

Where L_{Pt} is the platinum loading (mg/cm^2) and P_{Pt} is the weight percentage of metal supported on carbon (Pt/C).

Fig. 2.7 Schematic planar representation of the catalytic layer (A) At low Nafion content not all the catalyst particles are connected to the membrane by a Nafion bridge. (B) At the optimal Nafion content, there are good connections for ionic and electronic conduction for all the catalyst particles. (C) When there is too much Nafion, not all the catalyst particles are electronically connected to the diffusion layer (Passalacqua *et al.* 2001).

(d) Organic solvent

When the perfluorosulfonate-ionomer (PFSI), e.g. Nafion solution, is mixed with

organic solvent with different dielectric constant (ϵ), the mixture changes into one of the three stages: (i) solution ($\epsilon > 10$), (ii) colloid ($3 < \epsilon < 10$), and (iii) precipitation ($3 < \epsilon$). Uchida *et al.* (1995) reported that the maximum power densities of 0.45 and 1.08 W/cm² were achieved at 50 °C in a H₂/O₂ system at 0.1 and 0.59 MPa, respectively, when the catalyst ink was prepared with coprecipitation of Nafion colloid and simultaneous cross-linkage of Nafion covered on Pt/C in the butyl acetate organic solvent. Similar results were attained by shin *et al.* (2002). Their results showed that the colloidal method is preferred to prepare the ink for air brushing method as it forms 180 nm agglomerates bigger than those of conventional isopropanol solution method, which has a tendency to penetrate too far into the GDL to block the gas transport. Furthermore, the Nafion solution in the solution mode is easier to penetrate into the small pores below 0.07 μ m and cover the platinum particles. The effects of four different organic solvents with different dielectric constant, such as butyl acetate ($\epsilon=5.01$), iso-amyl alcohol ($\epsilon=15.8$), diethyl oxalate ($\epsilon=8.10$) and ethylene glycol ($\epsilon=38.66$), on the performance of PEM fuel cell were investigated using transfer printing method by Yang *et al.* (2004). It was found that the electrode prepared by using ethylene glycol showed the best performance of 840 mA/cm² at 0.6V in H₂/O₂ system compared with those prepared by other solvents. Nevertheless, because of the high decomposing temperature of ethylene glycol (196 °C) and dimethyl oxalate (163°C), the pores in the catalyst layers were partially filled with solvents after the heat treatment at 140°C of the electrodes. As a result, the transport of reactant gases through the electrode was decreased.

Glycerol is generally added into the paste to adjust the viscosity for improving paintability. In addition, it holds the carbon particles in suspension to minimize their

agglomeration during the ultrasonic procedure (Wilson and Gottesfeld 1992). However, according to the results from Chun *et al.* (1998), too much glycerol content (3:1 glycerol to 5% Nafion solution) in the catalyst slurry affects the performance of the thin film MEA at high current density of 350 mA/cm² and above. They suggested that high glycerol loading could reduce the contact area between the Pt electrocatalyst and Nafion, thus limiting the charge transfer. Paganin *et al.* (1996) brushed the catalyst slurry containing isopropanol instead of glycerol onto the gas diffusion layer to achieve the desired viscosity and hence improved good performance.

(e) Effect of unusual materials on CL structure and physical properties

The structural integrity of the thin film CL will decide the long-term performance stability of PEM fuel cell. Wilson *et al.* (1995) found that commercial Nafion can be converted to a thermoplastic form by ion-exchange of anionic group with large hydrophobic counter ions such as tetrabutylammonium (TBA⁺). The solubilized Nafion can be processed in a melted phase, which forms composite structure with high dispersion. As a result, high power density was achieved with Pt loading as low as 0.12 mg/cm² at the cathode with the maximum power loss of less than 10% in the 4000 h long-term operation. The SEM pictures obtained by Yoon *et al.* (2003) showed that the grain size in the CL increased when the Nafion ionomer was converted to the thermoplastic form by ion-exchange. Hence, it was not surprised to see that the MEA with TBA⁺ form showed markedly better performance than conventional MEA at high current region.

The effect of different pore forming additives on the porosity of the cathode catalyst layers was studied by Fischer *et al.* (1998) in both H₂/air and H₂/O₂ systems. They

fabricated their MEA using a hot spraying method which provided 35% porosity without any pore forming additive. The porosity was increased to 42% and 48% with the use of ammonium carbonate and ammonium oxalate as additives, respectively; while the porosity reached 65% when lithium carbonate was taken as the pore former. Their results showed that the additional porosity in the thin film CCL improved the air transport in the cathode, while the fine pore system without pore forming additives seemed to be easily flooded with water at high current density. The coarse pores can provide better water removal from the cathode, thus improving the utilisation of the catalyst in the electrodes. Anode drying is one of the challenges in the operation of PEM fuel cells. To better retain water in the anode, water absorbing materials such as silica and TiO_2 were added into the anode catalyst layer, which was called self-hydrating anode (Han *et al.* 2007). In their study, they dispersed the silica particles uniformly into the Nafion matrix to form Nafion-silica nano-composite. The optimal performance was achieved with silica loading of 6% in a single fuel cell operated without any external humidification. The achieved maximum power density was almost 1.6 times higher than that of a PEM fuel cell with a conventional anode. They confirmed that the self-hydrating anode enhanced the back-diffusion of water molecules in different extent from the cathode to the Nafion membrane of different thickness. Tang and Jiang (2008) exploited the silica self-humidifying anode by synthesizing nanosize mesoporous silica carbon supported Pt electrocatalyst through a hydrogen-bonding-assisted self-assembly route. The maximum power density reached 456 mW/cm^2 at elevated temperature of 100°C and low humidification of 30% RH, which was significantly higher than 345 mW/cm^2 for the cell with Pt/XC-72 carbon electrocatalyst.

Although the anode side requires the addition of water retention materials in the catalyst layer to prevent the dryness and increase the proton conductivity, the water removal from the cathode side, especially at high current density, is still a challenge for the conventional Nafion bound thin film cathode. The permeability of O₂ through water or Nafion in a short distance (less than 5 μ m) is sufficient for the reaction. But, this thin Nafion film tremendously limits the loading of catalyst which consequently diminishes the lifespan and stability of the electrode. Thus, one of the methods to control water transport and improve the gas transport is to add some hydrophobic and oxygen transferable materials into the cathode catalyst layer. Grot (Grot 2004) firstly claimed that when an electrode is coated with gas transport polymer such as perfluoroether (PFPE), it not only can promote water management in the PEMFC but also facilitate the transport of the reaction gas. Additionally, applying a coating of transport polymer to an electrode has the advantage of alleviating the carbon monoxide poisoning on the anode catalyst since the coating acts as a molecular sieve to pass the small hydrogen molecules but to block the ten times larger CO molecules. Dimethyl silicon oil (DSO) is another choice to improve the oxygen transportation and offer the hydrophobicity to the cathode in the PEM fuel cell. Since DSO meets the following criteria which are critical for the stable operation of a PEM fuel cell (Ji *et al.* 2009).

1. Chemically inert and thermally stable;
2. Much higher solubility of oxygen than in water. DSO is a nonpolarity molecule. A non-polar solvent has higher solubility for oxygen than a polar solvent. The solubility of oxygen in DSO is 0.168-0.190 mL/mL (25°C), while the solubility of oxygen in water is only 0.0171 mL/mL;
3. With high flash point and low freezing point. The operating temperature of

PEMFC covers a wide range from -20°C to high temperature (hot press at around 140°C). In this temperature range, its vapor pressure is relatively low.

4. With small surface tension so that the oil can easily permeate into small hole. Ji *et al.* (2009) exploited anti-flooding effect of the dimethyl silicon oil (DSO) on the cathode of a PEM fuel cell. They demonstrated that, even under fully flooded condition, the high oxygen flux in the DSO can still sustain the PEM fuel cell for much longer time than that with conventional cathode as shown in Figure 2.8. But they did not explain why the fuel cell with cathode loaded with DSO also collapsed at last under the running condition. The increased pore volume in the range of 20 nm - 70 nm with the addition of DSO in the cathode significantly enhances water removal from the cathode. As a result, the occupation of oil in the pore with diameter from 20 nm to 70 nm prevents serious flooding and assists the gas transport in the PEM fuel cell at high current density. To make a DSO loaded cathode, oil was firstly sprayed onto the catalyst layer of a conventional Pt/C electrode with micro porous layer. A small vacuum pump was then used to suck out the oil from the back layer to let the oil pass through the porous electrode, leaving some of oil in the catalyst layer and some of the oil in the gas diffusion layer. One main problem with this fabrication method for the anti-flooding electrode was the difficulty to control the quantity of the oil resided in the electrode.

Fig. 2.8 Cell voltage versus time of MEA with an anti-flooding electrode (AFE) and a conventional Pt/C electrode (CPE) cathode at a current density of 1 A/cm^2 , Test conditions: back pressure, $P_{O_2}=P_{H_2}=180 \text{ kPa}$; O_2 and H_2 flow rates are 150 and 160 sccm, respectively; Pt loading was 0.6 mg/cm^2 at both the cathode and anode; $T_{\text{cell}} = 60 \text{ }^\circ\text{C}$ (Ji *et al.* 2009)

2.3.2 Effect of gas diffusion layer on the liquid water dynamics

The porous gas diffusion layer (GDL) is one of the important components in PEM fuel cells which not only serves as the support structure for MEA but also transports electrons to and from the catalyst layers and ensures effective diffusion of reactants to the catalyst layers. The GDL also assists in water management by allowing an appropriate amount of water to reach the membrane for hydration as well as transporting the excess water out of the catalyst layer to the flow channel through the GDL. If the liquid water accumulates inside the GDL or CL, flooding will occur and significant gas transport limitation results. In order to mitigate the liquid water retention inside the pores of GDL, the GDL is often treated with hydrophobic

materials, such as PTFE, to change its wetting characteristics. Such treatment results in hydrophobic and hydrophilic pockets of pores in GDL. The hydrophobic regions are believed to provide pathway for gas transport whereas the hydrophilic regions facilitate the liquid transport (Mathias *et al.* 2003). Various techniques have been developed to treat the GDL with PTFE which includes dipping, brushing and spraying. A wide range of PTFE loading has been used, generally falling in the range of 5 wt % and 30 wt %.

Typically, there are two kinds of configurations for the GDL. One is called single layer GDL, which is a sheet of electrically conductive macro-porous non-woven carbon paper or a woven carbon cloth wet-proofed with (PTFE) coating. The single-layer GDL has macro-pores in its structure, allowing the effective transport of gas reactants to the catalyst layer. However, it gives rise to large contact resistance with the catalyst layer and poor physical support to the catalyst particles. Traditionally, this setup is unfavorable to water management in the fuel cell (Qi and Kaufman 2002). The other configuration of the GDL is referred as dual-layer GDL. A thin micro-porous layer (MPL) of the mixture of carbon black and PTFE is placed in between catalyst layer and conventional macro porous substrate. Because the water transport in the cathode is a two phase flow governed by capillary force, shear force and evaporation, the structural properties of the GDL, such as thickness, porosity, pore size distribution, wettability and fluid permeability, are critical factors for efficient water management.

(1) Effect of GDL materials and porosity on the water management

Carbon paper and carbon cloth are the most prevalent gas diffusion media used in PEM fuel cell. They both possess good mechanical strength, high electrical conductivity, and suitable porosity. However, GDL made by different manufacturers possesses different properties such as pore size distribution, air permeability, electronic resistance, thermal impedance and hydrophobicity in which the gas permeability and pore size diameter are the most important factors (Prasanna *et al.* 2004). For example, the mean pore diameters for Toray carbon paper TGP-H-60 and SGL are around 23 μm and 31.4 μm , respectively. In contrast to the random pore structure of the carbon paper materials, carbon cloth has typical pore diameter in the order of 6-8 μm . Thickness of GDL and its gas permeability play crucial role in oxygen mass transport when the mean pore size diameter is in the range of about 25-40 μm . GDL with larger pore size above 60 μm is prone to flooding in cathode compared to GDL with smaller pore diameter (Prasanna *et al.* 2004).

Spernjak *et al.* (2007) compared the effectiveness of Ballard woven carbon fiber 1071HCB, Toray carbon paper TGP-H-60, and SGL 31 carbon paper with 5wt.% PTFE. For untreated gas diffusion backing, water tends to climb up the channel sidewall instead of being expelled as discrete droplets from the pore openings. Under the same water production rate, water is trapped inside the cathode electrode for Toray paper. Ihonen *et al.* (2004) also confirmed that different gas diffusion backings possess various physical properties which lead to different flooding behaviors in the PEM fuel cell. The high clamping pressure, caused by the combined effect of decreased porosity and a temperature difference between GDL and current collector, increases the cell flooding. However, the relationship between physical properties of

GDL and fuel cell performance was not well established. Occasionally, different batches of GDL produced by same manufacturer showed substantially different behavior (Qi and Kaufman 2002).

Porosity of the GDL allows the reactant gases to reach the reaction zones and the water product to move out. It is one of the most important factors that influences the water and gas transport across the GDL. It not only determines the permeability for the gases and liquid water but also affects the liquid water saturation profile across the GDL and CL (Pasaogullari and Wang 2004). The pores smaller than the critical pore size will be filled with liquid water earlier, within the size range governed by the Kelvin equation (below several tens of nanometer), than the large pores, because water condensation will occur before the vapor pressure reaches saturation pressure at a given temperature. Hence, the smaller the pore-size and porosity, the larger the mass-transport will be. This was confirmed by the modeling simulations (Beyers *et al.* 1997). However, this phenomenon in the porous electrode will remain until the pressure difference across the liquid and vapor water interface becomes lower than the capillary pressure determined by the well-know Young –Laplace equation. Both theoretical (Bernardi and Verbrugge 1992) and experimental (Wilson *et al.* 1995) results show that it is not effective in ameliorating the water flooding problem if GDL only consists of the macropores only. The larger the pore, the greater the size of the droplet formed in the mouth of the pore will be, leading to higher oxygen diffusional barrier.

The effect of the porosity of GDL on the performance is mostly investigated by modeling, in which the porosity is often assumed for simplicity (Bernardi 1990;

Springer *et al.* 1993; Yi and Nguyen 1999; Um *et al.* 2000). However, the compression of the electrode on the solid landing area and water produced in the cathode can result in non-uniform distribution of the pores. Roshandel *et al.* (2005) simulated the effect of the porosity variation on the performance. They claimed that when the current density was low, the porosity variation in GDL had no significant influence on the level of polarization, whereas the influence was very significant at high current density. The non-uniformity of mass transport caused by the porosity variation limited the current density and lowered the performance. Similar results were also obtained by Chu *et al.* (2003), in which they concluded that even though a higher porosity in the GDL would lead to a higher consumption of oxygen, high porosity would lead to water flooding in the GDL, markedly decreasing the fuel cell performance. Zhan *et al.* (2006) simulated the water transport under steady-state conditions with a one-dimensional model. They found that the liquid water flux through the GDL increased with the increase of the contact angle and porosity and the decrease of the GDL thickness.

The effect of the porosity and pore distribution on the PEM fuel cell performance has also been explored experimentally. There are several methods that have been applied to change the porosity and pore distribution in the GDL (Kong *et al.* 2002; Deyrail *et al.* 2007; Han *et al.* 2008). A carbon-filled GDL (CFGDL) proposed by Han *et al.* (2008) showed a lower porosity of 67% and a much smaller average pore diameter of 4.7 μm compared to the conventional single layer GDL with porosity of 77% and pore diameter of 35.8 μm and dual-layer GDL with porosity of 73% and pore diameter of 25.5 μm . The largest limiting current density of the fuel cell with CFGDL was attributed to the fast removal of micro-water droplet formed in the micro pores of the

electrode. Kong *et al.* (2002) modified the macropore volume in the GDL by pore former Li_2CO_3 to reduce the mass-transport limitation, especially in the system with air as the oxidant. The performance improvement was attributed to the appropriate ratio of macropores and micropores co-exist in the GDL. Selvarani *et al.* (2008) have reported the use of sucrose as the pore former to manipulate the porosity of the diffusion layer and showed enhanced limiting current.

(2) Effect of the MPL on the water management

The introduction of MPL between the backing layer and CL is one of most popular methods to better remove water from the CL. The MPL is usually made of a mixture of carbon particles and PTFE. Thus, the macropore size is primarily determined by the size of carbon particle aggregates. For Vulcan CX-72, the primary particle size is about 30 nm and the aggregates formed by these primary particles are of micrometer size. Thus, the large pore dimension would be in the magnitude of microns in the MPL, and the pore size distribution should be quite uniform. The pore size range in MPL is around 0.1-0.5 μm compared to that of 10-100 μm for the backing layer. Water may not be able to form stable droplets inside of such small and hydrophobic pores (Qi and Kaufman 2002). It is thought that the MPL provides effective wicking of liquid water from the CL into the backing layer of the GDL, thereby reducing the tendency of electrode flooding (M. Mathias *et al.* 2003). Moreover, the MPL can provide a good physical micro-porous support for the catalyst layer and minimize the electrical contact resistance with the adjacent catalyst layer through better adhesion and contact between the various conductive components (Weber and Newman 2005). In addition, Qi and Karufman (2002) found that the MPL can diminish the difference among different carbon paper types made by different manufacturers or different

batches by the same manufacturer. However, the MPL in the GDL will increase the thickness and tortuosity and thereby the gas diffusion path for mass transport, which will decrease the effective diffusion coefficient of the GDL. Accordingly, the dual-layer GDL would have a large mass transport limitation than the single-layer GDL at a higher current density (Han *et al.* 2008).

A lot of efforts including both numerical and experimental methods have been put to investigate the effect of the MPL on the performance of a PEM fuel cell. Different experimental groups have shown that the use of MPL usually resulted in better performance of PEM fuel cell (Paganin *et al.* 1996; Passalacqua *et al.* 1998; Jordan *et al.* 2000; Janssen and Overvelde 2001; Qi and Kaufman 2002; Wang *et al.* 2006; Nam *et al.* 2009). Early in 1995, Wilson *et al.* (Wilson *et al.* 1995) claimed that the coarse pore structure of backing layer allowed for growth of large liquid water droplet, but the fine pore structure of the MPL limited their growth, thereby increasing the stability and power density of a fuel cell. Park *et al.* (Park *et al.* 2004) concluded that the sensitivity to the relative humidity condition could be dramatically eliminated by placing an MPL between the CL and backing layer. Therefore, the MPL plays an important role in water management with regard to stability as well as electrical conductivity. However, the explanation for this improvement is still a subject for debate, especially in terms of enhancing back-diffusion of water from the anode to the cathode by the MPL. Spornjak *et al.* (2007) visualized the water transport at the anode side using a transparent fuel cell with catalyst coated membrane (CCM). They concluded that the MPL at the cathode side created a pressure barrier for the water produced at the catalyst layer, so that the MPL could keep the membrane better hydrated under their operation conditions. Nevertheless, recently Atiyeh *et al.* (2007;

Karan *et al.* 2007) carried out a systematic experiments of net water drag with same CCM at 60 C under two different anode /cathode RHs (60/100% and 100/60%) and two stoichiometric ratios of H₂/air (1.4/2 and 1.4/3). They claimed that although the overall performance was improved by the presence of the MPL in the cathode, the fuel cell performance was not associated with the effect of overall net water drag.

On the other hand, modeling studies have been extensively carried out to investigate the mechanism of the MPL in water control and guide the experimental works. Early modeling studies were concerned with the influence of reactant stream humidification on water flooding using simple single gas phase transport (Nguyen and White 1993). Wang *et al.* (2001) simulated the polarization curve as well as water concentration distributions encompassing both single and two phase regimes of the air cathode. Nam and Kaviany (Nam and Kaviany 2003) found through half cell modeling that the placement of the MPL between cathode CL and backing layer helped in reducing water saturation in the adjacent CCL and enhancing water removal rate from the CCL to the cathode backing layer. Similar results was also obtained by Pasaogullari and Wang (2004). Later, Weber and Newman (2005) quantified the function of the MPL using two-phase flow and robust membrane model. As shown in Fig. 2.9, the best performance is achieved when only cathode electrode has a MPL in between the CL and carbon paper. They attributed the performance improvement to better oxygen transport and less ohmic resistance because of the higher structural stability, improved interlayer contact, and better catalyst-layer utilisation. They also claimed that the MPL acts as a valve that forces water away from the cathode side through membrane to anode, which is in contrast to the modeling results obtained by Nam and Kaviany (2003).

Fig. 2.9 The Polarization curve for three different cell arrangements: (dotted) No MPL, (dashed) symmetric MPLs and (solid) only cathode with MPL only. β is defined as the net water flux per proton flux through the membrane (Weber and Newman 2005)

The numerical study by Lin and Nguyen (2006) also showed that the PEM fuel cell with a MPL exhibited better performance than the fuel cells without a MPL in the cathode electrode. They hypothesized that the MPL keeps liquid water in the CL and increased the back-diffusion rate of water from the cathode the anode. Pasaogullari *et al.* (2005) developed a one-dimensional, two-phase model to study the function of the MPL including anode, cathode and the membrane. The results demonstrated that the hydraulic pressure build-up due to the strong capillary pressure in the MPL and the increased resistance to liquid water removal from the cathode resulted in a higher pressure differential across the membrane, which in turn promoted the water transport from cathode to anode. Although the back-flow of water was strongly dependent on several MPL parameters, such as hydrophobicity, thickness, pore size and porosity,

they claimed that the liquid saturation profile at the MPL and GDL interface was different due to a discontinuity of microporous and wetting characteristic, which reduced the water flux toward the cathode, thereby decreasing the cathode flooding and relaxing the mass transfer limitation. Recently, Kang and Ju (Kang and Ju 2009) developed a three dimensional numerical MPL model with the incorporation of the previously devised comprehensive and multi-phase fuel-cell models. They found that the liquid-entry pressure between an MPL and backing layer played important role in determining the function of the MPL. If the difference in the entry pressure was ignored, no benefit was shown with the MPL in the cathode. Only when a high liquid-entry pressure in an MPL was considered, the function of the MPL enhanced the back-flow of water across the membrane and then increased the fuel cell performance.

In summary, it is clear that MPL is able to improve the water management and enhance the performance of the PEM fuel cell. Although the explanation about the role of the MPL in water transport remains controversy, the advantages of the MPL appear to be widely accepted. Firstly, the saturated vapor pressure is higher inside the MPL than inside the backing layer due to smaller pore size and enhanced hydrophobicity. Hence the fuel cell with MPL in the cathode side is less prone to flooding. Secondly, the MPL renders the GDL more like a pressure valve with a two-fold function: pushing the water to the membrane side to effectively hydrate the membrane and providing a pressure buildup necessary to expel the water through the less hydrophobic backing layer into the cathode flow channels. The confusion on whether the role of a MPL is to enhance the back-diffusion of water from cathode to anode or to improve water removal from the CCL to support layer and flow channel

requires more investigations not only through numerical simulation but also through experiments.

(3) Effect of hydrophobicity and hydrophilicity of GDL on water management

The hydrophobic and hydrophilic properties of GDL play an important role in the performance of the PEM fuel cell. PTFE treatment has become a common industrial practice in preparing GDLs, which is introduced into the electrode structure in two stages during the electrode fabrication: support layer and MPL. The presence of PTFE in the gas diffusion layer serves three functions, i.e., binding the high surface carbon particles into a cohesive layer, forming channels, and imparting some hydrophobic character to the layer (Antolini *et al.* 2002). Higher PTFE content can lead to better hydrophobicity, but it will reduce the electrical conductivity. Furthermore, the diffusion is caught directly in the middle of the tradeoff between hydrophobicity and conductivity (Bevers *et al.* 1996). Hence, it is essential to optimize the content of PTFE with respect to the running conditions of the fuel cell. Numerous research papers aimed at developing GDLs with improved efficiency based on theoretical and experimental analysis (Shimpalee *et al.* 2007). Tüber *et al.* (2003) studied the water flooding issue in transparent PEM fuel cell with hydrophobic or hydrophilic GDL. Their results implied that the wetting property of the GDL directly influenced the accumulation of water produced in the gas channels of a transparent cathode at operating temperatures of around 30 C.

Park *et al.* (2004; 2008) investigated the water management in the GDL with and without MPL as the function of PTFE content and inferred that the capillary-force-driven water movement and the shear-force or vaporization-driven water

transportation should be considered carefully for all kinds of GDL structures. They indicated that PTFE increased the resistance of the water flow through the GDL due to the decrease of the MPL porosity and the increase of the volume fraction of hydrophobic pores. Thus, the optimized PTFE content resulted in an effective water control and improved oxygen diffusion kinetics in MEA. When humidified air was used as an oxidant, a maximum fuel cell performance was obtained with a PTFE loading of 20 wt.% at temperatures from 20 to 75 °C. Velayutham *et al.* also confirmed the same optimum concentration of PTFE in the MPL. But, for the GDL without MPL, the optimum content of PTFE was 23 wt.% in the GDL, which was slightly higher than that in the MPL under their operation conditions (Velayutham *et al.* 2007). Paganin *et al.* investigated the performance of the PEM fuel cells containing Vulcan XC-72R carbon black diffusion layers with varying PTFE contents and diffusion layer thickness. They tested the PTFE contents of 10, 15, 20, 30 and 40 wt.% in the diffusion layer and found that a diffusion layer containing 15 wt.% PTFE gave the best fuel cell performance (Paganin *et al.* 1996). Jiao and Zhou (2008) implied that different wettabilities of cathode could significantly affect liquid water flow patterns by employing a 3D, unsteady, two-phase flow model. They suggested that only the hydrophobic GDL could deteriorate the flooding of the catalyst layer and lower the performance of the PEM fuel cell.

The addition of PTFE not only modifies the wettability of the GDL to control the water transport, but also changes the porosity and structures of the GDL which are also very crucial for water control in the electrode. Giorgi *et al.* (1998) proposed that the content of PTFE affected the porosity of the diffusion layer, i.e., an increase in the PTFE content resulted in a decrease in the porosity of the diffusion layer. Lim and

Wang (2004) studied the effects of fluorinated ethylene propylene (FEP) hydrophobic polymer content in the GDL on the fuel cell performance. They suggested the crucial role of the surface morphology introduced by the hydrophobic content on the performance of the PEM fuel cell, i.e., the excessive FEP impregnation resulted in significant blockage of surface pores by thin FEP films and hence lowered the performance of the fuel cell. Similar conclusion was drawn by Guangyu and Trung (2005). They found that PTFE could enhance gas transport and water transport when a cell operates under flooding condition, but excessive PTFE loading could lead to a high flooding level in the catalyst layer. The optimal ratio of hydrophobic and hydrophilic pores is dependent on the pore size and its distribution. Zhou and Wu also confirmed the importance of the distribution of the fibers and the spatial mixed-wettability in the GDL using an equivalent capillary model of a microscale fiber-fence structure (Zhou and Wu 2010).

2.3.3 Membrane

Membrane is another key component in the PEM fuel cell. Nafion membrane is the most commonly used commercial perfluorinated ionomer membran. Fig. 2.10 shows the structure of Nafion. The proton conductivity of Nafion is strongly dependent on the water content inside the membrane (Fuller and Newman 1992; Zawodzinski Jr *et al.* 1993; Smitha *et al.* 2005). Therefore, the most general method to avoid the dehydration of membrane is to humidify the reaction gas. However, the humidification of the reactant gases significantly increases the risk of cathode flooding. There are three transport processes that associated with water and Nafion membrane which including the ionic conductivity, the water diffusion coefficient and

electro-osmotic drag coefficient (Doyle and Rahebdab 2003). Several efforts have been made to improve performance of Nafion to ascertain water retention especially at relatively higher temperatures. SiO_2 and TiO_2 are the most common particles incorporated into the Nafion to improve the water retention capability and to enable the operation of the fuel cell above 130 C (Chan *et al.* 2007; Wang *et al.* 2008; Lee *et al.* 2009). Mesoporous alumina (Al_2O_3) monolithic ceramic chips have also been incorporated into the Nafion membrane. However, proton conductivity varied linearly with relative humidity in Al_2O_3 , whereas a steep increase was observed for TiO_2 and SiO_2 between 58 and 81% relative humidity (Vichi *et al.* 1999).

Fig. 2.10 Structure of Nafion

2.3.4 Flow field design on flooding

Flow channel conducts reactant gases to MEA and removal excess water from MEA. Therefore, appropriate design of the flow field is also one of the most important parameters for water management (Zhang *et al.* 2006; Li *et al.* 2007; Zhu *et al.* 2007). A lot of investigations have been put to optimize the design of the flow channel including the flow patterns, channel ratios, wettability and surface roughness and so on (Cai *et al.* 2006; Ji *et al.* 2006; Zhu *et al.* 2008). Parallel flow field is the most conventional gas distribution method. However, it is not desirable of this design for the water management because diffusion is the dominant mechanism for the reactants

and products to travel to and from the electrode. Due to the very small pressure drop along the relatively short channels, the inadequate water drainage may block the channel, thus inducing non-uniformity of gas flow distribution which contributes to poor and unstable performance (Nguyen 1996; Mérida *et al.* 2001; Li and Sabir 2005). The interdigitated flow field, which consists of unconnected channel, was proposed by Nguyen to resolve the water flooding issue (Nguyen 1996). It is attractive since it overcomes mass transport limitation in porous electrodes by changing the diffusive mass transfer mechanism into a forced convective mass transfer. Furthermore, the shear force of the gas flow helps to remove a large amount of the liquid water out of the inner layers of the electrode, thereby effectively reducing the electrode flooding problem and significantly improving the cell performance at high current density operation (Wood Iii *et al.* 1998). Wang *et al.* (2007) found that the flow channel area ratio played an important role in achieving good fuel cell performance for both parallel flow and interdigitated flow channel.

Serpentine flow field, the most widely known and used channel design, is often regarded as the “industrial standard”, since PEM fuel cells with serpentine flow channels tend to have the best performance and durability/reliability under the same operating and design conditions (Li *et al.* 2007). However, serpentine flow channel has its own drawbacks which include parasitic power loss due to the substantial pressure drop along its relatively long reactant flow path and Nernst loss due to the significant decrease of oxygen concentration. In terms of the water management, the fuel cell with serpentine flow channel often suffers membrane dehydration near the channel inlet region and liquid water flooding near the channel exit because of excessive liquid water collected along the flow channel and carried downstream by the

reactant gas stream. These drawbacks increase the scale-up difficulties (Wang 2004). Through the simulation by a simplified conjugate-gradient method and a completely three-dimensional, two-phase, non-isothermal fuel cell model, Wang *et al.* (2009) claimed that the oxygen and liquid water transport in a single serpentine PEM fuel cell could be optimized by diverging channel heights and tapered channels. It should be emphasized that in addition to the flow channel layout, the wall surface morphology in the channel also plays an important role to control water in MEA. Cai *et al.* (2006) showed that although the water was moved faster on a hydrophobic surface, a hydrophobic channel side-wall was a disadvantage for the gas diffusion when the MEA had a hydrophilic surface. A hydrophilic channel side-wall with a hydrophobic MEA surface could avoid water accumulation on the MEA surface. He *et al.* found that both the different wetting condition and the roughness of the channel wall could affect the water transport behavior in the PEM fuel cell channel (He *et al.* 2010).

2.4 Summary of the literature review

Water transport within the cathode is one of the key issues to determine the performance of a PEM fuel cell. Water management in the cathode can be improved by optimizing the cathode structure, for example incorporation of micro-porous layer and controlling of cathode hydrophobicity. A structure-based model developed by Eikerling and Kornyshev (Eikerling and Kornyshev 1998) revealed the water handling ability of the cathode catalyst layer and its effect on the cell performance. More recently, Kraytsberg and Ein-Eli (Kraytsberg and Ein-Eli 2006) suggested that implementing cathode modified by oxygen permeable but water immiscible perfluorocarbons could help the water back diffusion to hydrate the membrane as

well as repel water out of the cathode. Due to the fact that the cathode catalyst layer is the location for electrochemical reaction and water production, one would expect that water management can be significantly improved in the cathode by optimizing the hydrophobicity of the cathode catalyst layer through the addition of hydrophobic dimethyl silicone oil (DSO) into the catalyst during the ink preparation. The motivation of this strategy is to combine the advantages of uniformly distributed Nafion in the Nafion-bonded electrode and the anti-flooding property in the PTFE-bonded electrode. Moreover, unlike the PTFE-bonded electrode, the fabrication of the DSO modified electrode does not require heat treatment, thus avoiding the agglomeration of the Pt/C catalyst.

Chapter 3. Experimental procedure

3.1 Chemicals and materials

The fuel cell catalysts, Nafion membranes, carbon papers and chemicals that were used in the experiments are listed as below: 50% Pt/C catalyst (Johnson Metthy, UK), carbon powder (Vulcan XC-72, Cabot Corporation, US), carbon paper (Toray TGPH-090, Japan), polytetrafluoroethylene (PTFE) dispersion (Teflon 30, 60% PTFE, Dupont Corporation, US), Nafion membranes (N112-117, EW1100, DuPont), dimethyl silicone oil (DSO, Shin-Etsu, Japan) ethanol (99.8%, sigma), sulfuric acid (95~97%, sigma), isopropanol (99%, sigma). Deionized water (Millipore Milli-Q, 18.2 M Ω at 25°C) was used in all the experiments. The morphology and phase composition of the 50% Pt/C catalyst are shown in Figure 3-1.

Fig. 3.1 TEM image (b) XRD pattern of the 50% Pt/C catalyst

3.2 Fuel cell preparation

The flowchart for the fuel cell preparation is shown in Fig. 3.2. Each step in the flowchart was detailed in the sub-sections below.

Fig. 3.2 Flowchart of the fuel cell electrode preparation

3.2.1 Catalyst ink preparation

The conventional catalyst ink was prepared by ultrasonically dispersing carbon-supported 50 wt.% Pt catalyst (Johnson Matthey, UK) into a mixture of Nafion solution, deionized water and isopropanol. The dry Nafion content in the ink was controlled to be 30 wt% for both anode and cathode. For the DSO-modified cathode catalyst ink, DSO (Shin-Etsu, Japan) was firstly emulsified into a mixture of deionized water and isopropanol by a highly intensive ultrasonic machine (Vcx 750, Sonics, USA) with appropriate loading. A homogeneous ink suspension was then obtained by ultrasonically mixing the Pt/C catalyst and 30 wt% dry Nafion solution into above mixture.

3.2.2 Carbon paper pretreatment

The water-proof carbon papers were prepared by a three-step process. First, the carbon paper was dipped into the acetone for 1 hour to ensure that the carbon fibers were clean and that the paper was dust free. The second step was to slowly immerse the untreated carbon papers (Toray TGPB-090) into a PTFE solution for 5 min under gentle stirring, and then dry them in an oven at 80-100°C. Subsequently, the PTFE treated carbon papers were sintered at 250°C for 30 minutes to evaporate water content and impurities, followed by sintering at 350°C for another 30 min to form a thin layer of PTFE film on the carbon paper. After cooling down to room temperature, the water-proof carbon papers were ready for use. The PTFE loadings in the water-proof carbon papers were determined by the mass difference of the carbon papers before and after the PTFE treatment. The PTFE loading was about 13% for the water-proof carbon papers used in this study.

3.2.3 Preparation of micro-porous layer and catalyst layer

The micro-porous layer (MPL) was fabricated right on the top of the PTFE-treated carbon paper. Firstly, the carbon black powder (Cabot Vulcan XC72R) was ultrasonically dispersed in a solution of deionized water and isopropanol at room temperature. Then, 10 wt.% of PTFE dispersion was added into the slurry drop by drop under vigorous stirring. After well mixing, the carbon black ink was painted onto the surface of the PTFE-treated carbon paper. Finally, the MPL was sintered at 250°C and 350°C for 30 minutes each. The loading of the carbon black and PTFE in the MPL were around 1 and 0.3 mg/cm², respectively.

Once the catalyst ink was ready as described in Section 3.2.1, the anode catalyst layer was prepared by evenly painting the anode catalyst ink onto the MPL with Pt loading of 0.4 mg/cm², followed by baking at 80°C for 2 hours. The anode electrode was ready for the fabrication of membrane electrode assembly (MEA). In order to study the effects of the hydrophobicity of the cathode catalyst layer on the cathode water management and the fuel cell performance, two kinds of backing layers, PTFE-treated carbon paper and PTFE-treated carbon paper with MPL, were used to prepare the cathode electrodes. The fabrication procedure for the cathode catalyst layer was the same as that of the anode catalyst layer.

3.2.4 Nafion membrane treatment

The purpose of Nafion membrane treatment was to remove any impurities and improve the protonic conductivity during operation. Firstly, the newly-bought Nafion membrane 112 (EW1100, DuPont) with desired dimensions was sequentially soaked in deionized water at 80°C for 30 minutes, 5% hydrogen peroxide solution at 80°C for 30 minutes, deionized water at 80°C for 30 minutes, 0.5 M sulfuric acid at 80°C for 30 minutes, and finally deionized water at 80°C for 30 minutes. The membrane was then left in deionized water until cooling down to room temperature. Finally, the treated membrane was kept in deionized water to avoid dehydration and re-contamination.

3.2.5 Membrane electrode assembly

A membrane electrode assembly (MEA) is the core component of a PEM fuel cell, which is a sandwiched configuration of anode electrode/Nafion membrane/cathode electrode. To prepare the membrane electrode assembly, the anode and cathode electrodes with dimension of 2.2 cm × 1.8 cm were put on the both side of a treated Nafion membrane with the catalyst layer in contact with the membrane. This sandwich structure was placed in between two large aluminum plates and hot-pressed at 140°C with a pressure of 50 kg/cm² for 2 min. The final membrane electrode assembly should be bonded together rigidly to ensure good contact between the electrode and the Nafion membrane.

3.3 Experimental setup

The single fuel cell includes a MEA (anode/Nafion membrane/cathode), sealing silicon gaskets, fuel and oxidant flow channels and cell interconnects. The graphite bipolar plates in the single cell have serpentine channels for the distribution of reactant gases. Current collecting stainless steel plates are attached behind the graphite blocks. Fig. 3.3 shows the schematic of single cell assembly. The overview of the fuel cell test setup is shown in Fig. 3.4, which is composed of a single fuel cell and a fuel cell control system. The effective working area of the single fuel cell used in this study is 4.14 cm^2 ($2.2 \text{ cm} \times 1.8 \text{ cm}$). As illustrated in Fig. 3.5, the fuel cell control system can control the fuel cell operating temperature, humidification temperature and the gases flow rate. After the MEA is mounted in the fuel cell fixture, fuel (hydrogen) and oxidant (air or oxygen) are supplied to the anode and cathode, respectively. The gas flow rates of the fuel and oxidant are controlled by two digital mass flow meters. Before feeding into the fuel cell, the gases were passed through an external humidifier which controls the degree of relative humidity of the fuel and oxidant. A temperature regulator is employed to control the fuel cell temperature. The desired operating temperature is regulated by pumping constant hot water through the fuel cell.

Fig. 3.3 Schematic of single fuel cell assembly

Fig. 3.4 Overview of the fuel cell test setup

- 1 two-stage pressure regulating valve
- 2 mass flow meter
- 3 humidifier
- 4 fuel cell
- 5 pressure meter
- 6 temperature sensor
- 7 electrochemistry test station (Solartron)
- 8 water bath heater
- 9 separator
- 10 back pressure valve

Fig. 3.5 Schematic of the fuel cell control system

3.4 Electrochemical characterization

Understanding the physicochemical characteristics of PEM fuel cells is very important for the fuel cell research and development. The electrochemical characterization is a key procedure to evaluate and optimize the fuel cell performance and understand the fuel cell reaction mechanisms. Several electrochemical techniques, such as cyclic voltammetry, steady-state polarization and electrochemical impedance spectroscopy (EIS), were applied to characterize the single fuel cell. All of the characterizations were carried out in a Solartron Electrochemical Interface (1255B) in conjunction with a Solartron Frequency Response Analyzer (1287).

3.4.1 Fuel cell polarization and performance

The performance of a PEM fuel cell is usually evaluated by determining the polarization and power density curves of the cell. These curves provide the behaviour of the fuel cell performance at a glance and an assessment of its optimal operating conditions (temperature, humidity, electrocatalyst, ion-exchange membrane). The potential vs current density measurements of the fuel cell were conducted in H_2/O_2 and H_2/air systems under a pressure range of 1 to 2 atm from room temperature to 80°C. The flow rates were adjusted according to the output current in order to keep a constant air/fuel stoichiometry of 2.

3.4.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance is usually measured by applying an excitation AC potential to an electrochemical cell and measuring the response current through the cell. The excitation potential expressed as a complex function can be described as,

$$E(t) = E_o \exp(j\omega t) \quad (3-1)$$

and the response current is,

$$I(t) = I_o \exp(j\omega t - j\phi) \quad (3-2)$$

The impedance is then represented as a complex number,

$$Z = \frac{E}{I} = Z_o \exp(j\phi) = Z_o (\cos \phi + j \sin \phi) \quad (3-3)$$

The AC behaviors of an electrochemical system can be represented by a conventional equivalent circuits consisting of passive components, which are often used to understand the impedance response. The impedance data is commonly presented in the form of Nyquist diagram, plotting real component of impedance on x-axis while the imaginary part on y-axis. Fig. 3.6 shows a typical impedance spectrum of a fuel cell system and its corresponding equivalent circuit. The high-frequency intercept of the impedance arc on the real axis, R_Ω , which is dominated by the membrane resistance, represents the total ohmic resistance of the cell. Meanwhile high frequency resistance R_p , well known as the effective charge transfer resistance, is largely contributed by the rate of the interfacial oxygen reduction process, the protonic conductivity and the oxygen permeability limitations within the CCL. The value of this resistance is equal to the diameter of the capacitive arc and determines the size of the arc.

Fig. 3.6 A typical Nyquist diagram of a fuel cell system and its corresponding Equivalent circuit

The main advantage of EIS in fuel cell characterization is its ability to resolve the individual limiting process in the different frequency domain, e.g. resolution of ohmic loss, kinetic loss and mass transport loss in the overall PEM fuel cell power losses. This ability provides more information than the steady-state experiments for a better understanding of the factors: such as electrode composition and structure; membrane characteristics; operating parameters (cell temperature, humidification, gas composition, pressure). Due to the negligible overpotential loss of the anode, the *in situ* impedance measurements of fuel cells are normally performed in a two-electrode configuration with the anode serving both as the counter and the reference electrode. Impedance spectra were recorded at frequencies range of 0.01 Hz to 10k Hz with AC amplitude of 10 mV and superimposed DC bias. Wet hydrogen and air/O₂ were fed into the anode and cathode, respectively. The ohmic, activation and mass transport losses can be obtained by fitting the impedance spectrum with the equivalent circuit.

3.5 Physical Characterization

3.5.1 Transmission electron microscope (TEM)

The Pt/C catalyst was examined by a transmission electronic microscope (TEM, JEOL 2010). Pt/C was ultrasonically dispersed into isopropanol to form a suspension, which was then dropped onto copper grid coated with carbon film and dried at room temperature.

3.5.2 Scanning electron microscopy (SEM)

The morphology of the carbon paper and catalyst layer was observed under scanning electron microscopy (SEM) (JSM-5600, JEOL, Japan). The electrodes were fractured after immersing in liquid nitrogen to observe the cross section. The SEM images can provide microstructural information of surface roughness and structure, catalyst layer/carbon paper interface, and homogeneity of the catalyst layer.

3.5.3 Mercury porosimetry

Pore size and distribution of all the electrodes were measured by a Mercury intrusion porosimetry (Autopore 9500, Micromeritics Inc.). Cumulative pore volume as a function of pore diameter was determined from the mercury intrusion data, i.e. the volume of mercury penetrating the pores versus the applied pressure. Under the assumption that all pores are cylindrical, the pore diameter d can be calculated from the amount of mercury uptake and the applied pressure P expressed by the Washburn equation:

$$d_p = -\frac{4\sigma \cos \theta}{P} \quad (3.4)$$

where d_p is the pore diameter, P is the applied pressure, σ the surface tension of mercury and θ the contact angle between the mercury and the sample. The volume of mercury penetrating the pores is measured directly as a function of applied pressure. The measured intrusion volume and pressure were used to calculate pore size, pore volume and pore volume distribution. The surface tension and contact angles of mercury used in the calculations were 480 dynes/cm and 140°, respectively.

3.5.4 Contact angle measurement

Contact angle measurement is a simple-to-adopt method for surface analysis related to the surface energy and tension. Typically, it uses a sample stage to hold the substrate, a syringe to apply a droplet of liquid, a light source to illuminate the droplet, and a set of optics for magnifying the image for observation. The profile of the water droplet was revealed by the images taken by the CCD camera. The contact angles of the catalyst layers (CL) of the PEM fuel cells in this study were measured at room temperature to understand the wetting property of the CL and the effect of the DSO on the hydrophobicity of the CL. Because of the slow dynamic response of the dry Nafion electrolyte for the water absorption, the profile of the water droplet was recorded immediately after applying the water droplet on the CL and after 1 hr incubation of the droplet on the CL at room temperature.

Chapter 4.Characterization of DSO-modified cathode catalyst layer in PEM fuel cells

4.1 Introduction

Although the importance of the GDL in preventing flooding has been extensively studied, the role of the cathode catalyst layer (CCL) on fuel cell water balance has never been investigated in depth, either experimentally or numerically. Traditionally, the cathode catalyst layer was considered as an ultra thin layer to shorten the distance of the gas diffusion and to facilitate water transport. Most cell and stack model treat CCL as infinitesimally thin interface without structural resolution when dealing with the flooding problem because of the complexity of CCL (Eikerling 2006). Only few efforts have been put to investigate effect of the properties of cathode catalyst layer on the PEMFC performance. The structure-based model revealed that the CCL is a critical fuel cell component in view of flooding that could give rise to limiting current behavior. The CCL can act as watershed in fuel cell to regulate the balance between the liquid water and vapor. Jiao and Zhou (2008) numerically showed that different wettability in both CCL and GDL could affect liquid water flow patterns significantly, thus influencing the performance of the cell.

It was simulated that modifying the cathode with oxygen permeable but water immiscible perfluorocarbons would divert the water flow from CCL to electrolyte (Kraytsberg and Ein-Eli 2006). In order to understand the effect of the CCL on the water management and performance of the PEM fuel cell, hydrophobic dimethyl

silicone oil (DSO) was used to modify the physical properties of the CCL. The surface morphology, elemental analysis, surface wettability, and pore size distribution, were characterized by SEM, Energy-dispersive X-ray spectroscopy (EDX), contact angle measurement and porosimeter, respectively. The electrochemical impedance spectroscopy (EIS) was carried out to fundamentally understand the mechanisms of the water transport within the cathode. The well known thin-film/flooded-agglomerate model was employed to distinguish the sources of the performance loss in the PEM fuel cell. Some parameters such as contact angle obtained from this study could be used to validate the fuel cell models and guide the CCL design for the PEM fuel cell.

4.2 Experimental

The carbon-supported Pt catalyst is 50 wt. % Pt/C (Johnson Matthey) with the average Pt diameter of about 2 nm. All electrodes consisted of a wet-proofed carbon paper as the backing layer and a CL. Commercial TGP-H-090 carbon papers were impregnated with 15% PTFE to make it hydrophobic and used as cathode GDLs. An appropriate DSO (Shin-Etsu, Japan) was emulsified into a mixture of water and isopropanol by a highly intensive ultrasonic machine (Vcx 750, Sonics, USA) with appropriate loading. Then, the catalyst ink was prepared by ultrasonically dispersing the carbon-supported Pt catalyst and Nafion solution into the above emulsion. For the normal cathode, same procedure was applied to make the ink except that there was no DSO in the mixture of water and isopropanol. The content of Nafion in the catalyst layer was 30 wt. %. To better understand the effect of DSO on cathodic water management, no MPL was fabricated. The Pt and DSO loading were calculated from

the total loading and from the weight percentage of Pt in the electrode. The loading of Pt in the CL with and without DSO was 0.35 mg/cm^2 and with a Nafion loading of 0.56 mg/cm^2 . The commercial Nafion 112 membrane (EW1100, DuPont) was treated according to the recommended procedure by the supplier. The MEA was prepared by hot-pressing the anode (without any DSO) and cathode (with DSO) onto the both sides of the Nafion 112 membrane at 140°C and a pressure of 50 kg/cm^2 for 2 min.

4.3 Results and Discussion

4.3.1 Morphology analysis from SEM observation

Fig. 4.1 SEM image for the cross-section of the interfacial region between the catalyst layer and GDL

Fig. 4.2 SEM images of the top-view for carbon paper TGP-H-090 before (a) and after (b) PTFE treatment

The cross-section of the CCL/GDL interface was characterized by scanning electron microscopy (SEM) and is presented in Fig. 4.1. The image revealed that the CCL has a uniform thickness around 10 μ m on the wet-proofed carbon paper. This ensures similar property of the wet-proofed carbon paper after being applied with catalyst ink, so that the effect of the hydrophobicity of the cathode catalyst layer on the fuel cell performance can be investigated without any ambiguity. Fig. 4.2 shows the SEM images of TGP-H-090 carbon paper before and after the hydrophobic treatment (PTFE immersion). The microstructure of carbon paper TGP-H-090 is characterized by a non-woven structure with many macro-open pores formed by multiple intersecting graphite fibers. After treated with PTFE (wt 10%), the structure of graphite fiber is strengthened and the surfaces become more hydrophobic. It appears in the SEM image that a number of pores near the surface are blocked by thin PTFE films, especially for small pores, which was also reported by Bevers *et al.* (1996).

Fig. 4.3 SEM images of the CCL surface with different DSO loadings: (a) no DSO; (b) 0.25 mg/cm² DSO; (c) 0.4 mg/cm² DSO; (d) 0.5 mg/cm² DSO; (e) 0.65 mg/cm² DSO

Fig. 4.3 shows the top-view of the cathodes with different DSO loadings from 0 (normal cathode) to 0.65 mg/cm^2 DSO in the CCL. Before examining the morphology by the SEM, the samples were vacuumed to remove the DSO droplets from the CCL. The SEM images in Fig. 4.3 indicated that the DSO droplets in the CCL functioned as pore former. Without DSO in the CCL (the normal cathode), the CCL surface was quite compact with uniform and fine pore size of less than $0.3 \text{ }\mu\text{m}$. The pore size increased obviously with the increase of the DSO loading in the CCL. For example, for the CCL loaded with 0.5 mg/cm^2 DSO, a great number of big pores with diameter around $1\text{-}3\text{ }\mu\text{m}$ were homogeneously distributed on the surface of the CCL. According to the magnified SEM images shown in Fig. 4.4, it was believed that the DSO droplets might fill up the big pores with diameters of $1\text{-}3\text{ }\mu\text{m}$ in the CCL. This phenomenon was also confirmed by the porosimetric measurement. When the DSO loading was increased to 0.65 mg/cm^2 , the ratio of pores with diameters of $1\text{-}3\text{ }\mu\text{m}$ was further increased.

Fig. 4.4 Magnified SEM images of the CCL surface: (a) the CCL without DSO and (b) the CCL with 0.5 mg/cm^2 DSO

4.3.2 EDX analysis

In order to study the effect of the CCL on the water management, no MPL was interposed between the CL and the GDL in this study to avoid possible ambiguity. Without the MPL support, the penetration of catalyst particles into the GDL could cause significant catalyst loss and alter the GDL properties. Thus, a technique for ink preparation and painting the slurry onto the wet-proofed carbon paper was developed in this study to minimize the penetration of the catalyst into the carbon paper. This was confirmed by the cross-section observation shown in Fig. 4.1 and the EDX analysis illustrated in Fig. 4.5.

(a)

(b)

Fig. 4.5 EDX analysis for the catalyst layer surface (a) and back face of cathode loaded with 0.5 mg/cm^2 DSO

The EDX analyses on the top surface of the CCL loaded with 0.5 mg/cm^2 DSO showed the presence of Pt, C, F, Si and S. The chemical elements, Pt and C come from the Pt/C catalyst, and F and S from Nafion solution. Apparently, Si is from the remains of DSO. The EDX analyses on the back face of the same sample showed different results. Only three elements C, F and S were detected. It is not surprised to observe F on the back face of the cathode electrode since the carbon paper was treated with PTFE. As reported in literature, Nafion molecule can easily penetrate through the carbon paper to the back face (Cheng *et al.* 1999). Hence, the observed element S in Fig. 4.5 (b) could be from the Nafion ionomer which crosses through the carbon paper. This Nafion crossover to the back face of electrode may cause some part of GDL to be hydrophilic. No Pt was detected on the back surface of the electrode, meaning no catalyst particles have penetrated into the carbon paper and dropped to the back of the electrode.

4.3.3 The contact angle measurements

Liquid water transport through the cathode catalyst layer relies strongly not only on the pore structure, porosity and permeability but also on the degree of hydrophobicity. In this study, the hydrophobicity of the cathode catalyst layer was varied by adding hydrophobic DSO into the cathode catalyst layer during the catalyst ink preparation stage. The images of the water droplet on the two kinds of cathodes, i.e., normal cathode and cathode with DSO loading of 0.5 mg/cm^2 , were taken and compared in Fig. 4.6. Initially, the surface contact angles for both cathodes are almost the same at around 130° (shown in Fig. 4.6a and 4.6b). However, after one hour incubation of the water droplet on the CCL, the surface contact angle of the normal cathode

significantly decreased from 130° to around 70° , which was much smaller than the value of 101° of the CCL with DSO loading of $0.5\text{mg}/\text{cm}^2$.

Fig. 4.6 Images of water droplet: initial water droplet on (a) normal cathode catalyst layer and (b) $0.5\text{ mg}/\text{cm}^2$ DSO loaded cathode catalyst layer; water droplet after one hour on (c) normal cathode catalyst layer and (d) $0.5\text{ mg}/\text{cm}^2$ DSO loaded cathode catalyst layer

Nafion comprises of hydrophobic reticulated structure and percolated hydrophilic regions, which becomes hydrophobic when it is dry (Brack *et al.* 2004). As a result, the normal cathode initially exhibited hydrophobic property when water droplet was just applied onto the cathode catalyst layer (Fig. 4.6 a). However, because water gradually hydrates the hydrophilic regions, the cathode CL finally turns to be hydrophilic (Fig. 4.2c). The surface contact angles of various cathodes with different DSO loadings of 0, 0.25, 0.40, 0.50 and $0.65\text{ mg}/\text{cm}^2$ were summarized in Fig. 4.7. The error bar in Fig. 4.7 was based on the surface contact angles measured from three cathodes with same DSO loading. Initially, the measured contact angles for all of the

cathodes are similar and around 130° . After one hour incubation of the water droplet on the cathode catalyst layer, the surface contact angle significantly decreased with the reduction of the DSO loading in the cathode catalyst layer. The results in Fig. 4.7 clearly revealed that the addition of DSO significantly enhances the hydrophobicity of the cathode catalyst layer.

Fig. 4.7 Contact angles of the cathode catalyst layers with different DSO loadings measured at initial time and after one hour

4.3.4 Pore size distribution analysis

The porosity and pore size distribution are very important parameters for the design of gas diffusion electrode, since they significantly affect the transport of reactants/products in the electrode. Fig. 4.8 (a) shows the cumulative pore volume vs. pore size for normal cathode and cathode loaded with 0.5 mg/cm^2 DSO. It is clear that, for both cathodes, the cumulative pore volume increased sharply between pore diameters of $10 \text{ }\mu\text{m}$ and $100 \text{ }\mu\text{m}$, whereas at small pore diameter below $10 \mu\text{m}$, the

cumulative pore volume increased gradually and then remained rather constant. This implied that most of the pores were located in the macro-porous substrate (MaPS). Only small portion of the pores were in the catalyst layer. The results also clearly show that the cathode loaded with 0.5 mg/cm² DSO has slightly higher cumulative pore volume in the CCL than the normal cathode. The differential pore volume ($dV/d\log d_p$) for normal cathode and cathode loaded with 0.5 mg/cm² DSO is illustrated in Fig 4.8 (b).

The intrusion curves show two zones which have critical boundaries at ca. 10 μm . The SEM images in Fig 4.3 show that most of the pores in the CCL were less than 10 μm . Combining the SEM observation with results from cumulative pore volume vs. pore size, we may conclude that the pores larger than 10 μm are from the carbon paper. For normal cathode, the intrusion curve shows small peaks in pore size distribution at *ca.* 0.005 μm , 0.011 μm , 0.040 μm and 1.6 μm . It was reported that the catalyst layer has two distinctive pore distributions with a boundary of *ca.* 0.03 μm . The smaller pores (primary pores) were identified with the space in the agglomerate working as a reaction volume, and the larger pores (secondary pores) were spaces between the agglomerates as the main gas channels in the electrode of the PEM fuel cell (Uchida *et al.* 1995).

(a)

(b)

Fig. 4.8 (a) The cumulative volume for the normal cathode without MPL and the cathode loaded with 0.5 mg/cm^2 DSO without MPL; (b) Pore size distribution

The highest peak of the pore distribution for the normal cathode catalyst layer was found to be at *ca.* 0.005 μm with differential pore volume of 0.15 cm^3/g . This was probably consistent with the pores between closely packed carbon particles inside the agglomeration (Ihonen *et al.* 2002). The pore distribution curve for the cathode loaded with 0.5 mg/cm^2 DSO exhibits fluctuation behaviour between the pore size of 0.004 μm and 5 μm , indicating that the DSO can create pores between the agglomerates in the CCL.

The appearance of the peaks for the pores smaller than 10 nm in the DSO loaded cathode (Fig. 4.8 (b)) indicated that DSO can penetrate into the pores between the carbon particles in the agglomerate. In general, the pores with a diameter below 20 nm may always be occupied by water due to water capillary condensation in such small pores. Ji *et al.* (2009) reported that condensation of water in the pores with a diameter from 20 to 70 nm resulted in cathode flooding. Since the oxygen diffusion in the DSO is more than 20 times higher than that in the water (Merkel *et al.* 2000), the penetration of DSO into the aggregates is beneficial to prevent water from condensation while maintaining high oxygen transport rate to the reaction sites. Water can be easily expelled from the pores with diameters over 70 nm because of their hydrophobicity. As a result, a great amount of pores with diameters from 40 nm to 5 μm created by the addition of DSO, which has a contact angle of 117°, are able to significantly improve water removal from the CCL.

CHAPTER 4 CHARACTERIZATION OF DSO-MODIFIED CATHODE
CATALYST LAYER IN PEM FUEL CELL

Table 4.1 The pore characters of the normal cathode and the cathode loaded with 0.5 mg/cm² DSO

Samples	Total porosity	Average pore diameter (μm)	Local porosity		Media pore diameter (μm)	Average pore diameter (μm)	
			Less than 5 μm	Larger than 5 μm		Less than 5 μm	Larger than 5 μm
Normal cathode	76%	0.3179	7.41%	68.59%	28.7	0.649	51.632
Cathode loaded with 0.5 mg/cm² DSO	79%	0.2973	11.02%	67.98%	28.2	0.653	51.632

To estimate the extent of variation in pore-size distribution for the normal cathode and the cathode loaded with 0.5 mg/cm² DSO, the variation in the bulk porosity ε , local porosity, media pore diameter and the average pore diameter are summarized in Table 4-1. ε was calculated from the ratio of the total pore volume to the bulk volume of the electrode as shown in Eq. (4-1). While $d_{p,avg}$ was determined by Eq. (4-2) based on the Carman-Kozeny theory (Kaviany 1991). The local porosity was defined as the ratio of the volume of pores in a certain size range to the bulk volume of the electrode.

$$\varepsilon = \frac{V_{tol}}{V_{bulk}} \quad (4-1)$$

$$d_{avg} = \frac{4V_{tol}}{A_{bulk}} \quad (4-2)$$

where V_{tol} and V_{bulk} denote the total pore volume and the bulk volume in the electrode, respectively. A_{bulk} is the total pore surface area in the GDL. With the addition of 0.5 mg/cm² DSO in the CCL, the total porosity has improved from 76% to 79%, while the local porosity corresponding to the pores less than 5 μm has increased from 7.41% to 11.02%.

4.3.5 Electrochemical characterization

(1) General pattern of the electrochemical impedance spectroscopy (EIS)

The electrode behaviors in the PEM fuel cell are quite complex and influenced by several factors, including electrode composition, structure and the hydration level within the CL and polymer membrane (Springer *et al.* 1996; Yuan *et al.* 2007). EIS has been demonstrated to be a powerful experimental technique to investigate not only the electrochemical performance of the PEM fuel cell, but also the mechanisms of the water management in the fuel cell. The impedance spectra of the fuel cell with cathode loaded with 0.5 mg/cm² DSO were recorded at various cell voltages and presented in Fig. 4.9 (a). At cell voltages higher than 0.6V, the impedance spectra only showed a high-frequency (HF) intercept, R_{Ω} , and a depressed arc with diameter of, R_p , which means that the mass transport limitation is almost negligible under such operating conditions. Due to the negligible overpotential loss of the anode, the higher frequency arc reflects the effective charge transfer resistance at the cathode and the double-layer capacitance within the catalyst layer. The effective charge transfer resistance, R_p , is largely contributed by the rate of the interfacial oxygen reduction process, the protonic conductivity and the oxygen permeability limitations within the CCL.

The high-frequency intercept of the impedance arc on the real axis, R_{Ω} , represents the total ohmic resistance of the cell, which can be expressed as the sum of the contributions from contact resistances between components, R_c , and ohmic resistances of the cell components such as the membrane, R_m , catalyst layer, R_{cat} , gas diffusion layer, R_{back} , and bipolar plates, R_{bi} (Yuan *et al.* 2007):

$$R_{\Omega} = R_c + R_m + R_{cat} + R_{back} + R_{bi} \approx R_m \quad (4-3)$$

With the decrease of the cell voltage, the total ohmic resistance decreased sharply and kept unchanged at the cell voltage lower than 0.5 V as shown in Fig. 4.9 (b). This phenomenon could be due to the changes of membrane hydration level at these cell voltages. As seen in Eq. (4-3), R_m is the ionic resistance and is the main contributor to the total ohmic resistance of the fuel cell. Since there is no humidification in the cathode, the membrane hydration is strongly dependent on the water product in the cathode which increased with the decrease of the cell voltage. When the membrane was fully hydrated by the water product in the cathode, the total ohmic resistance reached a constant. In other words, the performance of a PEM fuel cell operating at low current density is strongly affected by the humidification in the cathode even in room temperature.

When the cell voltage was lower than 0.6V, an additional arc appeared at low frequency range. The low frequency loop provides information on diffusional processes which is also important to determine the fuel cell performance at high current density. However, the origin of this loop was controversial in literature, i.e. the loop was believed to be the slow diffusion of oxygen through the backing layer (Springer *et al.* 1996), the back diffusion of water in the membrane (Paganin *et al.* 1998) , or the diffusion of water in the catalyst layer (Wagner *et al.* 1998). In this study, the appearance of the low frequency arc in Fig. 4.9 with the decrease of the cell voltage could be due to the drop of O_2 concentration within the CCL at higher cell current densities. The diffusion limitations in the cathode affect the O_2 partial pressure both statically and dynamically at the backing/catalyst layer interface (Springer *et al.* 1996).

(a)

(b)

Fig. 4.9 (a) Impedance spectra obtained at various cell voltages for the fuel cell with $0.5\text{mg}/\text{cm}^2$ DSO loaded cathode using humidified H_2 as fuel and dry air as oxidant, respectively. (b) The dependence of R_{Ω} on E_{cell}

The effect of humidification on the EIS patterns was studied at voltages of 0.8V and 0.4V with different humidification conditions. Fig. 4.10 presents the impedance spectra for both humidification in hydrogen and air (bh), only fuel humidification (fh)

and no humidification in hydrogen and air (nh). It is obvious from the results in Fig. 4.10 that the effective charge transfer resistance R_p and ohmic resistance for the fuel cell without any humidification were much larger than the fuel cell with other humidification conditions at 0.8 V. The trends were also reported by other researchers (Ciureanu and Roberge 2001). The humidification of reactants could increase (i) the hydration of membrane, thus reducing the membrane ohmic resistance which was confirmed by the decrease of the ohmic resistance in the sequence of nh>fh >bh; (ii) proton conductivity of Nafion in the catalyst layer due to presence of water; and (iii) the theoretical open circuit potential for oxygen reduction E_{eq} as expressed in Eq. (4-4).

$$E_{eq} = 1.23 + \frac{RT}{nF} \log \frac{p_{air} x_{O_2}}{1 - f_{liq}} \quad (4-4)$$

where x_{O_2} is the fraction of the oxygen, f_{liq} the fraction of liquid water, F Faraday constant, R universal gas constant.

As demonstrated in Fig. 4.10, various humidification conditions also have different effect on the impedance spectra of the fuel cell at the cell voltage of 0.4V. At this voltage, the ohmic resistances were almost the same for the fuel cell operated at different humidification conditions, meaning that the membrane was fully hydrated by the water product at 0.4 V even without any external humidification. However, the polarization resistance of the fuel cell with both humidification in the anode and cathode was found to be the largest among the studied conditions. The low frequency loop significantly increased at 0.4 V with both humidification in the anode and cathode, illustrating that serious water flooding happened in the cathode and the diffusion process dominated the fuel cell performance. With only humidification in the anode, the lowest polarization resistance was observed at 0.4 V although a low

frequency loop appeared due to the oxygen diffusion within the cathode. The results suggested that a fuel cell with DSO loaded cathode can achieve the highest performance under high current density at room temperature only if the fuel is humidified.

Fig. 4.10 Effect of humidification on cell impedance spectra at cell voltages of 0.8 V and 0.4 V for the fuel cell with cathode loaded with 0.5mg/cm^2 DSO (a) Both humidifications in the anode and cathode (b) Only humidification in the anode (c) No humidification in the anode and cathode

The impedance spectra in Fig. 4.9 (a) were fitted to the nonlinear least-squares procedure (NLSQ) using the equivalent circuit shown in Fig. 4.11. For the spectra with only one loop, the used equivalent circuit contained only the series combination of R_l and (R_2 , CPE1), as shown in Fig. 4.11 (a). R_l is the total ohmic resistance of the cell R_Ω . CPE1 is a constant phase element, while R_2 stands for the charge-transfer resistance. A simple equivalent circuit containing a series of two parallel RC circuits was used to fit the EIS spectra that have two arcs obtained at cell voltages lower than 0.6 V. Except for the ohmic resistance R_l , the other components in the circuit account only for the cathode due to the negligible overpotential loss of the anode. R_3 and CPE2 stand for a diffusional process in the low frequency range (Ciureanu and Roberge 2001).

Fig. 4.11 Equivalent circuits for impedance spectra with one arc (a) and two arc (b)

(2) Theoretical analysis of the EIS

The diameter of the higher frequency arc R_p as a function of E_{cell} was obtained by fitting the EIS spectra and plotted in Fig. 4.12. The charge transfer resistance R_p was found to decrease from $2.73 \Omega\text{cm}^2$ to $0.25 \Omega\text{cm}^2$ with the cell voltage decreasing from 0.8 V to 0.6 V. This reflects the accelerating driving force for the interfacial oxygen

reduction process, which can be determined by the Tafel Equation as follows:

$$I = Ai_o \exp\left(\frac{(1-\alpha)nF}{RT}\eta\right) \quad (4-5)$$

Where I is the current density, η overpotential, A electrode surface area, i_o exchange current density, F Faraday constant, R universal gas constant, α : symmetry factor.

Fig. 4.12 The dependence of effective charge transfer resistance on E_{cell} for the fuel cell with 0.5mg/cm^2 DSO loaded cathodes using humidified H_2 as fuel and dry air as oxidant

However, the diameter of this higher frequency arc reached a minimum value at cell voltage of 0.6 V and subsequently increased when the cell voltage further decreased from 0.6 V to 0.3V. The dependence of the effective charge transfer resistance arc on the cell voltage shown in Fig. 4.12 has also been observed by other researchers, which can be satisfactorily explained by the thin film/flooded agglomerate model of the catalyst layer (Springer and Raistrick 1989; Ciureanu and Roberge 2001; Park *et al.*

2006). In this model, the cathode catalyst layer was assumed to contain porous agglomerates of the polymer electrolyte (Nafion) and the carbon-supported Pt particles. The open hydrophobic channels provide diffusion paths for the gaseous oxygen from the bulk to the catalyst particles, where the charge transfer reaction takes place at the three-phase boundary. The agglomerated zones with a thickness L_y are filled with electrolyte and covered at the outside with a thin layer of pure electrolyte (of thickness δ).

Springer and Raistrick firstly proposed this model and gave the full mathematical derivation in 1989 (Springer and Raistrick 1989). Based on this model, Ciureanu and Roberge (2001) derived a simple diagnostic equation for R_p as follows:

$$\frac{R}{R_0} = 2 \frac{1 + \Gamma e^{\psi} \gamma}{(\sigma + \gamma) e^{\psi}} \quad (4-6)$$

$$\Gamma = \frac{\delta k_0}{D_f} \quad (4-7)$$

$$\Phi = \left(\frac{k_0 L_y}{D_a} \right)^{1/2} \quad (4-8)$$

$$\gamma = \frac{\tanh \Phi e^{\psi/2}}{\Phi e^{\psi/2}} \quad (4-9)$$

$$\sigma = \sec h^2 (\Phi e^{\psi/2}) \quad (4-10)$$

Where Γ is the parameter defining the thin film diffusion and Φ is the agglomerate diffusion parameter. R Resistance obtained from the low frequency limit ($\omega \rightarrow 0$); R_0

Resistance at limiting current density; $\psi = \eta_c \frac{\alpha F}{\Re T}$ the dimensionless overpotential; α

the transfer coefficient, F the Faraday constant, η_c the cathodic overpotential, R the gas constant, T the absolute temperature, D_f and D_a the diffusion coefficient of oxygen

in the electrolyte film and in the agglomerate, respectively.

According to Eq. (4-6), depending on the cathodic overpotential, the CCL was found to be responsible for two types of mass transport limitations for ORR: the progressive depletion of oxygen within pores (agglomerate diffusion) and oxygen diffusion through the thin Nafion layer (thin film diffusion). At low overpotential, the oxygen diffusion through the agglomerate pores process is dominant and high frequency resistance continuously decreases with the increase of ψ . However, at high overpotential, the thin film diffusion becomes non-negligible, thus increasing the high frequency resistance. Gradually, the thin film diffusion becomes predominant with the further increase of the cathodic overpotential. As shown in Fig. 4.12, Eq. (4-6) can fit quite well to the experimental R_p as a function of cell voltage by taking the values of Φ and Γ as 3×10^{-4} and 4×10^{-5} respectively, which are comparable with Φ and Γ as 3.8×10^{-4} and 4.7×10^{-4} adopted by Park *et al.* (Park *et al.* 2006). This confirms that thin film/flooded agglomerate dynamics in the catalyst layer is responsible for a high-frequency arc in the impedance spectra. The existing turnaround cell voltage at 0.6 V indicates that the electrode kinetics is controlled by agglomerate diffusion above 0.6 V, while thin film diffusion acts as a rate-determining step below 0.6 V.

(3) Effect of DSO in catalyst layer on the impedance spectra

Fig. 4.13 shows the impedance spectra for the fuel cells with the cathode loaded with 0.5 mg/cm^2 DSO and the normal cathode operating in pure oxygen at different cell voltages. It can be found that the high frequency arc drops in magnitude with decreasing the cell voltage, e.g. increasing the cell over-potential, for the fuel cell with a cathode loaded with 0.5 mg/cm^2 DSO. However, for the fuel cell with a normal

cathode, the high frequency arc slightly reduces with the cell voltage decreasing from 0.8 V to 0.7 V. Then, a low frequency arc starts to appear when the cell voltage further decreases to 0.6 V.

Fig. 4.13 Impedance spectra obtained at various cell voltages for the fuel cells with (a) the cathode loaded with 0.5mg/cm² DSO and (b) the normal cathode using humidified H₂ as fuel and dry O₂ as oxidant

As mentioned above, the effective charge transfer resistance R_p (the high frequency arc) could be contributed by the rate of the interfacial oxygen reduction process, the protonic conductivity and oxygen permeability limitations within the catalyst layer. As explained by Eq. (4-6), two types of mass transport consisting of oxygen diffusion within pores (agglomerate diffusion) and oxygen diffusion through the thin Nafion layer (thin film diffusion) could determine the magnitude of charge transfer resistance R_p . When the cathodic overpotential is low, e.g. in the condition of high cell voltage, the agglomerate diffusion predominates. As a result, the charge transfer resistance R_p

decreases sharply with the increase of cell overpotential or the decrease of the cell voltage. However, the charge transfer resistance increases with the decrease of the cell voltage due to the dominance of the thin film diffusion. The addition of DSO into the CCL can modify the hydrophobicity around the agglomerate zone, easily repelling the water product out of the CCL. As a result, the DSO loaded cathode can provide more diffusion paths than the normal cathode for oxygen through the open hydrophobic channels so as to increase the agglomerate diffusion within the CCL. For the normal cathode, the open pores in the CCL are prone to retain the water product, resulting in the dependence of oxygen transport on the thin film diffusion.

To better understand how the micropores and hydrophobicity of the CCL affect the fuel cell performance, a series of experiments were performed and the impedance spectra were recorded for the fundamental analysis. Fig. 4.14 presents the EIS spectra at cell voltage of 0.8 V for the fuel cells with the normal cathode and cathodes loaded with different amount of DSO in dry oxygen/humidified hydrogen system. It is obvious from the results that the Nyquist plots for all of the fuel cells with different cathodes show only a kinetic loop under low overpotential condition (e.g. high cell voltage). The charge transfer resistance R_p was found to increase with the increase of the DSO content in the CCL. With the mechanisms discussed in Section 4.3.5.3, the dependence of effective charge transfer resistance R_p on the DSO loading in the CCL can be explained by thin film/flooded-agglomerate model. At high cell voltage such as 0.8 V, water accumulation within the cathode is not a main concern. As a result, the thin film diffusion is negligible (Ciureanu and Roberge 2001) and the oxygen diffusion process is dominated by agglomerate diffusion in the catalyst layer (through the open pores in the agglomeration). Since some open pores have been occupied by

the liquid DSO, oxygen agglomerate diffusion through the open pores has been partially replaced by the diffusion through the DSO. Therefore, according to Eq. (4-6), the charge transfer resistance R_p decreases with the increase of the DSO content.

With further reducing the cell voltage, higher current was generated and more water was produced within the cathode catalyst layer. If the water product cannot be effectively removed from the cathode catalyst layer, cathode flooding will happen. As shown in Fig. 4.15, the EIS spectra are distinctively changed for the fuel cells with different cathodes at 0.4 V compare to those at 0.8 V in dry air/humidified hydrogen system. All of the impedance spectra for the fuel cells with different cathodes exhibit two loops with R_p in the order: $R_{p,normal} > R_{p,0.25} > R_{p,0.65} > R_{p,0.4} > R_{p,0.5}$. This trend could be due to the balance between the agglomerate diffusion and the flooded thin film diffusion in the cathode catalyst layer. Appropriate amount of DSO could efficiently remove water out of the reaction zone to facilitate oxygen transport. However, too much DSO is not beneficial to oxygen transport due to the occupation of the liquid DSO in the open pores. For the fuel cells with the normal cathode and the cathode loaded with 0.25 mg/cm² DSO, the low frequency loop started to distort due to the dominance of the oxygen transport within the CCL. This, on the other hand, indicated that the fuel cells with a normal cathode or the cathodes with very low DSO content would suffer serious flooding problem at high current density (Yuan *et al.* 2006). Since all of the fuel cells with different cathodes had the same backing layers, the different results observed in Fig. 4.14 and 4-15 could be attributed to the different water transport mechanisms within the CCL. It can be concluded that appropriate water management in the CCL is also a key factor to optimize the cathode and, ultimately, improve the fuel cell performance.

Fig. 4.14 EIS obtained at 0.8 V for the fuel cells with a normal cathode and the cathodes with different DSO contents with humidified H₂ as fuel and dry oxygen as oxidant

Fig. 4.15 EIS obtained at 0.4V for the fuel cells with a normal cathode and different DSO loaded cathodes using humidified H₂ as fuel and dry air as oxidant

Chapter 5. Effect of DSO in cathode catalyst layer on the performance of PEM fuel cell

5.1 Introduction

In this chapter, the effects of hydrophobicity of the cathode catalyst layer on the performance of the PEM fuel cells were studied through the addition of hydrophobic dimethyl silicone oil (DSO) into the cathode catalyst layer. Conventionally, PTFE was selected to bind the catalyst and at the same time provide the appropriate hydrophobicity to the open pores, thus avoiding water blocking which is desirable for gas diffusion. Although this property is uniquely desirable, the necessary heat treatment of the electrode at around 350°C resulted in the agglomeration of the Pt/C catalyst and the consequent reduction of the catalyst utilization (Cheng *et al.* 1999). In addition, because Nafion was impregnated into the PTFE-bonded electrode, the catalyst utilization and the cell performance were strongly dependent on the Nafion distribution within the catalyst layer (Passalacqua *et al.* 2001). A performance penalty was paid for the decrease in humidity of Nafion and possible blocking of the proton or electron pathway in the catalyst, which would lead to poor utilization of the catalyst (Ticianelli *et al.* 1988).

Commonly, the thin-film electrode design, which has been found to achieve twice the power density output compared with that of the PTFE-bonded catalyst layers (Litster and McLean 2004), is popularly employed to avoid the problems and loss due to the addition of PTFE in the cathode catalyst layer (Ticianelli *et al.* 1988; Wilson and

Gottesfeld 1992; Wilson *et al.* 1995). However, in the thin film catalyst layer, the gas was not provided with a network of hydrophobic pores as in the PTFE-bonded catalyst layer. Thus, the gas diffusion through the catalyst layer must traverse pores filled with water and/or ionomer (Wilson and Goffesfeld 1992).

In this study, the hydrophobicity of the cathode catalyst layer was provided by adding the hydrophobic DSO into the catalyst ink mixture during the preparation. The motivation of this strategy was to combine the advantages of uniformly distributed Nafion in the Nafion-bonded electrode and the anti-flooding property in the PTFE-bonded electrode. Moreover, unlike the PTFE-bonded electrode, the fabrication of the DSO modified electrode did not require any heat treatment, thus avoiding the agglomeration of the Pt/C catalyst. To explicitly demonstrate the effect of hydrophobicity of the cathode catalyst layer on the water management, no MPL was interposed between the CL and the GDL to avoid possible ambiguity. The loading of the DSO in the cathode catalyst layer was optimized experimentally to achieve the best fuel cell performance. Finally, this optimized cathode was applied in a self-breathing PEMFC (SB-PEMFC) stack using Polymethylmethacrylate (PMMA) as the fuel cell fixture. The cathode flooding in a SB-PEMFC stack is often a concern at high current density, since water is difficult to be removed by free convection in the air. With the use of the anti-flooding DSO loaded cathode, our SB-PEMFC stack achieved good performance with improved stability and likely prolonged life span.

5.2 Experimental

The MEAs were fabricated following the procedure described in Chapter 4 and tested

using an in-house made fuel cell fixture, which has a geometric area of 4.14 cm^2 and single-serpentine flow channel cut into the graphite bipolar plates. The channel is 0.8 mm in width and 1 mm depth, with 0.8 mm wide lands. Gases were humidified by passing through a temperature-controlled water bath. Hydrogen and air/O₂ were fed into the anode and cathode, respectively, at a stoichiometry of 2.1 calculated at 1 A/cm^2 . Without specifying, all tests were carried out at room temperature of around 22°C and at atmospheric pressure. The steady-state polarizations were measured using the Solartron Electrochemical Interface (1255B). To fabricate an self-breathing stack, an infrared CO₂ laser (Universal M-300 Laser Platform, Universal Laser Systems Inc., Arizona, USA) was used to engrave microstructures directly on the PMMA substrate.

5.3 Results and discussion

5.3.1 Performance at room temperature

(1) Steady-state I-V polarization

The performance losses in the PEMFC cathode, especially when the fuel cell is operated with air as oxidant, are significant due to the following factors: (i) limited interfacial oxygen electrochemical kinetics, (ii) limited protonic conductivity through the CCL, and (iii) limited effective permeability of oxygen in the CCL. It has been confirmed that a high-performance cathode should have good gas access to the electrocatalyst as well as sufficient protonic conductivity within the CCL. The hydration condition within the CCL has a profound influence on electrode performance. In order to investigate the effect of DSO in the cathode catalyst layer on

the polarization behaviors of a single fuel cell, MEAs with the same anode but different cathodes (with DSO loading of 0, 0.25, 0.40, 0.50 to 0.65 mg/cm² in the cathode catalyst layer) were fabricated and tested. The normal cathode, which has no DSO in the cathode catalyst layer, was used for comparison. Fig. 5.1 shows the effects of DSO loadings in the CCL on the fuel cell polarization curves obtained at room temperature and atmospheric pressure under humidified hydrogen and dry air.

To understand the operational stability of the fuel cells under testing conditions, the polarization behaviors right after half an hour of gas purging and after running at constant voltage of 0.4 V for 3 hours were recorded and compared for all of the fuel cells with different MEAs. During the IV sweeping right after half an hour of gas purging, the CCL and the membrane were under dry condition, thus expecting an under-saturation condition in the cathodes. As a result, two phenomena can be observed from the polarization curves shown in Fig. 5.1a. One was the low output current density at voltage of 0.8 V for all the MEAs, which could be due to the low ionic conductivity of the Nafion cluster in the CL right after half an hour of gas purging. More specifically, the output current densities at 0.8 V were found to be 56, 50, 41, 26, 12 mA/cm² for the MEAs with DSO loading of 0, 0.25, 0.40, 0.50 to 0.65 mg/cm² in the CCL, respectively. With the loading of DSO increasing, the current densities at 0.8 V decreased significantly. The other phenomenon was the similar limiting current densities observed for the MEAs except for the one with 0.5 mg/cm² DSO loaded cathode. This could be attributed to the optimized balance between the improved cathode hydrophobicity for water expelling and the blocking effect of the liquid DSO within the cathode for the fuel cell with cathode loaded with 0.5 mg/cm² DSO.

Fig. 5.1 Polarization V-I curves obtained at room temperature and atmosphere pressure with humidified hydrogen and dry air (a) I-V sweeping right after 30 mins of gas purging; (b) I-V sweeping right after the fuel cell running at a constant voltage of 0.4 V for 3 hours and (c) corresponding maximum power density

As shown in Fig. 5.1b, after running the fuel cells at a constant voltage of 0.4 V for 3 hrs, the kinetic polarization of the fuel cells has been greatly improved due to the enhanced Nafion conductivity and catalyst utilization by opening up many “dead” regions in the CL when some water present in the pores of CL (Eikerling and Kornyshev 1998; Qi and Kaufman 2002). However, fast drop of the I-V curve at high current density was observed for the fuel cell with normal cathode after polarization at a constant voltage of 0.4 V for 3 hrs. During the I-V sweeping right after the gas purging, the fuel cell with normal cathode showed a limiting current density of 741 mAcm⁻², which significantly dropped to ~320 mA cm⁻² after further polarization at a constant voltage of 0.4 V for 3 hrs. The surface contact angle measurement shown in Fig. 4.6 revealed that the normal cathode turned to be hydrophilic after 1 h of incubation in water due to the gradual hydration of the Nafion clusters in the catalyst layer. As a result, the liquid water produced during the constant voltage polarization would occupy the hydrophilic pores in the CCL, thus causing serious flooding in the normal cathode and preventing the oxygen transport from bulk into the cathode catalyst layer (Li *et al.* 2008). The addition of DSO increased the hydrophobicity of the cathode catalyst layer, which was believed to be able to help expel water from the voids of the CL and facilitate the hydration of PEM (Jiao and Zhou 2007). This was confirmed by the polarization curves for the fuel cells with DSO loaded cathodes shown in Fig. 5.4b. It was found that the limiting current densities of the fuel cells with cathodes loaded with DSO of more than 0.4 mg/cm² remained almost unchanged before and after 3 hrs of constant voltage polarization, which were significantly different from the cells with cathodes loaded with DSO of less than 0.4 mg/cm². The comparative results in Fig. 5.1a and Fig. 5.1b together with the contact angle results in

Fig. 4.6 clearly indicated that the flooding phenomenon in the cathode could be effectively prevented by increasing the hydrophobicity in the cathode catalyst layer.

Fig. 5.1c compares the maximum power densities of the fuel cells with different cathodes right after half an hour of gas purging and after 3 hrs of constant voltage polarization at 0.4V. The results showed that the maximum power densities measured in the IV sweeping right after the gas purging were slightly different. However, the maximum power densities of the fuel cells with normal cathode and cathode loaded with 0.25 mg/cm² DSO significantly dropped from 290 mW/cm² to 144 mW/cm² and 295 mW/cm² to 201 mW/cm², respectively after 3 hrs of constant voltage polarization. However, obvious increase in the maximum power density was observed for the fuel cell with cathode loaded with 0.50 mg/cm² of DSO after 3 hrs of constant voltage polarization. The optimal DSO loading was found to be 0.50 mg/cm² with the highest maximum power density of 356 mW/cm² among the fuel cells in this study. Referring back to the polarization curves in Fig. 5.1a and 5.1b, one can understand that the changes of the maximum power densities of the fuel cells are mainly attributed to the electrolyte hydration and oxygen transport in the cathode. For the normal cathode, the serious flooding in the cathode led to the drop of the power density. With excessive DSO loading in the cathode catalyst layer (e.g. the case of 0.65 mg/cm² in this study), even though no flooding phenomenon was observed after polarization, a lower limiting current density of ~750 mA/cm² was observed when compared to that with optimal loading of 0.50 mg/cm². This indicated that excessive DSO content in the cathode catalyst layer would result in blockage of some voids and hence a restricted surface area for reactant transport, which causes lower limiting current density.

The effects of DSO in the cathode catalyst layer on the fuel cell performance were also investigated using humidified hydrogen and dry oxygen as the oxidant at room temperature (Fig. 5.2). The fuel cells with cathodes loaded with 0, 0.25, 0.40, 0.50 and 0.65 mg/cm² DSO showed current densities of 613.5, 785.8, 936.2, 961.1, 830.5 mA/cm² at 0.6 V, respectively. An improvement of 80% in the current density at 0.6 V was observed for the fuel cell with cathode loaded with 0.50 mg/cm² DSO compared to that of the fuel cell with normal cathode.

Moreover, the fuel cells with DSO loaded cathodes showed limiting current densities close to ~2000 mA cm⁻², which was around 1.7 times higher than that of the fuel cell with normal cathode. To make the results comparable, all of the fuel cells were tested at a stoichiometry of 2.1 calculated at 1 A/cm². The appearance of the limiting current for the fuel cell with 0.50 mg/cm² loaded cathode was due to the low stoichiometry number of oxygen, which means that almost all oxygen provided has been consumed in the cathode. Those results indicated that, if the hydrophobicity of the cathode catalyst layer was carefully optimized, not only the flooding problem could be avoided but also the catalyst utilization would be improved. The maximum power densities in humidified hydrogen and dry oxygen at room temperature were found to be 400, 551, 666, 709, 602 mWcm⁻² for the fuel cells with cathodes loaded with 0, 0.25, 0.40, 0.50 and 0.65 mg/cm² DSO, respectively.

Fig. 5.2 Polarization V-I curves (a) and power densities (b) of the single PEMFCs with normal cathode and cathodes with different DSO content in humidified hydrogen and dry oxygen at room temperature and atmosphere pressure

(2) Transient analysis of water management in CCL of PEM fuel cell

The conflicting requirements of electrolyte hydration and electrode anti-flooding should be met to achieve high performance of the PEM fuel cells. Events such as start-up, changes in operating conditions, changes in electrical loading, etc, can affect the water balance within the fuel cell, thus causing variation of the fuel cell output. In this section, transient analysis is conducted to study the water management issue in the CCL of a single fuel cell with different cathodes. The dynamic responses of the fuel cell upon the potential steps were recorded to interpret the effects of DSO loadings in the CCL on the water management, e.g. hydration and dehydration of the electrolyte and water flooding in the fuel cells.

Fig. 5.3 The potential step pattern used to characterize the fuel cells

Fig. 5.4 Dynamic responses of the fuel cells with different cathodes in humidified hydrogen and dry air at room temperature under voltages of 0.8V

Fig. 5.5 Dynamic responses of the fuel cells with different cathodes in humidified hydrogen and dry air at room temperature under voltages of 0.6V

Fig. 5.6 Dynamic responses of the fuel cells with different cathodes in humidified hydrogen and dry air at room temperature under voltages of 0.4V

Fig. 5.7 Dynamic responses of the fuel cells with different cathodes in humidified hydrogen and dry air at room temperature under voltages of 0.1V

The potential steps for the transient analysis are patterned in Fig. 5.3 with time period of 1 hr, 1 hr, 2.5 hr and 1 hrs at 0.8 V, 0.6 V, 0.4 V and 0.1 V, respectively. The potential step experiments were carried out at room temperature (22°C) and atmosphere pressure with humidified hydrogen and dry air feed into the anode and cathode, respectively. In order to ensure the initial hydration of the electrolyte to be fully saturated, the potential steps were started immediately after 4 hrs of polarization at 0.4 V. The dynamic responses of the single fuel cells with normal cathode and cathodes with different DSO loadings were recorded and presented in Fig. 5.4-5.7.

As shown in Fig. 5.4, when the potential stepped down from OCV to 0.8 V, several phenomena can be observed: (i) the dynamic responses are in time scales from 10 to 50 min; (ii) the output current density gradually decreased after the potential step for all of the fuel cells; (iii) the higher the DSO loading in the CCL, the lower the steady-state current density will be; (iv) the higher the DSO loading in the CCL, the longer the time required for the fuel cell to reach a steady-state. Benziger *et al.* studied the sorption dynamics of Nafion membrane (Benziger *et al.* 2005). They found that it takes around 1000 s for a saturated Nafion 1110 membrane to complete the water desorption process at 30°C. The time scales of the dynamic responses in Fig 5.4 were consistent with their study, indicating that the dehydration of the electrolyte could be the main reasons for the observed phenomena. Because of low output current density at potential of 0.8 V, the water produced by the electrochemical reaction was insufficient to sustain the initial hydration of the electrolyte. As a result, the electrolyte gradually dehydrated, increasing the ohmic resistance of the fuel cell and reducing the output current density. Furthermore, the CCL with hydrophobic DSO was more effective to expel water from CCL to gas flow channel through the GDL

than the normal CCL. The higher DSO loading in the CCL, the lower the water retention ability of the CCL will be, speeding up the dehydration process of the electrolyte.

Different dynamic responses are observed in Fig. 5.5 when the potential further stepped down from 0.8 V to 0.6 V. Two stages can be clearly seen from the dynamic responses, i.e. the current density initially increased to a maximum value, and then gradually decreased to a steady state value. Table 5-1 summarizes the information of the dynamic responses as a function of the DSO loadings in the CCL. It can be found that the higher the DSO loading in the CCL, the longer the time required for the fuel cell to reach the maximum current density. Also, the fuel cell with normal cathode experienced significant current drops from a maximum value of 530 mA/cm² to a steady state current of 290 mA/cm². These observations can be explained by the two consecutive processes happening in the fuel cell during the potential step, e.g. the initial hydration of the electrolyte and the subsequent water flooding in the cathode. When the potential stepped down from 0.8 V to 0.6 V, initially, sufficient water is produced to hydrate the dehydrated electrolyte, reducing the ohmic resistance and increasing the output current density. With the time elapse, excessive water is produced, resulting in the electrode flooding and causing performance deterioration of the fuel cell.

Table 5.1 Information obtained from the dynamic responses in Fig 5.5

DSO loading (mg/cm²)	Time to reach maximum current (min)	Steady state current (mA/cm²)	Time to reach steady state current (min)
0	0.42	293	6.37
0.25	0.92	445	5.33
0.4	1.76	446	5.51
0.5	1.77	508	6.17
0.65	1.4	361	7.71

As shown in Fig. 5.6 and 5.7, when the potential further stepped down from 0.6 V to 0.4 V and 0.1 V, the fuel cells can reach a steady state condition rather quickly. The fuel cell with normal cathode exhibited much lower steady state current density. For example, at potential of 0.1 V, the steady state current density was around 1000 mA/cm² of the fuel cell with cathode loaded with 0.5 mg/cm² DSO, which was 3 times more than that of the fuel cell with normal cathode. One can conclude from the results that the incorporation of hydrophobic DSO in the CCL can effectively expel water out of cathode, thus alleviating the water flooding in the fuel cell and significantly improving fuel cell performance at high current density. However, as shown in Fig. 5.8, one should bear in mind that this benefit is paid by scarifying the fuel cell performance at low current density.

Fig. 5.8 Steady-state output current densities at various cell voltages as a function of DSO loadings in the CCL of the PEM fuel cell

In order to further understand the effects of DSO in the cathode catalyst layer on the fuel cell performance, the start-up behaviors of the fuel cells with normal cathode and cathode loaded with DSO 0.5 mg/cm^2 were investigated under dry hydrogen and dry air condition at room temperature. The dynamic responses of the fuel cells at 0.4 V were recorded for comparison. Because dry hydrogen and dry air were fed into the fuel cell, the Nafion membrane and the Nafion clusters in the electrodes showed extremely low ionic conductivity due to the dehydration, leading to negligible initial output currents (shown in Fig. 5.9). For the fuel cell with normal cathode, the current density increased significantly to a maximum value of 600 mA/cm^2 within 1 min, then gradually dropped to around 450 mA/cm^2 . However, quite different start-up behavior was observed for the fuel cell with a cathode loaded with 0.5 mg/cm^2 DSO, i.e., (i) it

required around 5 min to reach a maximum current of 750 mA/cm²; (ii) no obvious current dropped was observed over a period of more than 30 min.

Fig. 5.9 Effect of DSO in the cathode catalyst layer on the start-up behaviors of the fuel cells in dry hydrogen and dry air at room temperature (at 0.4 V)

The different start-up behaviors of the fuel cells with normal and with DSO loaded cathodes could be caused by the different hydrophobicity in the cathode catalyst layers. Because of the hydrophilic property of the normal cathode, the Nafion in the normal cathode is easier to be hydrated by the water produced during operation than that of the hydrophobic DSO loaded cathode (Sena *et al.* 1999). As a result, the fuel cell with a normal cathode can reach a maximum current within much shorter time than that with DSO loaded cathode. However, the hydrophilic property of the normal cathode at the same time causes it to be easily flooded during operation, which is reflected by the drop of the current after 1 min of operation shown in Fig. 5.9. Thus, although the

fuel cell with DSO loaded cathode showed a slower start-up time in dry hydrogen and dry air, it demonstrated an excellent anti-flooding ability at high current condition.

(3) Stability testing

The stability of the fuel cells was studied by running the fuel cell in humidified hydrogen and dry air at room temperature for 40 hrs. The output current densities of the fuel cells were recorded at a constant cell potential of 0.4V. The results are presented in Fig. 5.10. The output power density at potential of 0.4 V corresponds roughly to the maximum power density and yields 34% voltage efficiency. Although the fuel cells are more efficiently operated at higher potentials (e.g., 48% efficiency at 0.7 V), operating at condition near the maximum power density was to observe the overall fuel cell performance under demanding life-test conditions. It can be seen from the results that all of the fuel cells can run stably over the 40 hrs operating period. The current density for the fuel cell with cathode loaded with 0.5 mg/cm² DSO was 3 times higher than that of the fuel cell with normal cathode. For the same mechanisms discussed above, the fuel cells with DSO loaded cathodes demonstrated current increment during the first 2 hrs of operation.

Fig. 5.10 Stability of the fuel cells with different cathodes at voltage of 0.4 V in humidified hydrogen and dry air at room temperature

5.3.2 Effects of operating temperature on the fuel cell performance

The effects of the DSO loadings in the cathode catalyst layer on the performance of a PEM fuel cell at room temperature have been investigated and characterized systematically in the previous Sections and Chapter 4. An optimal DSO loading was found to be 0.5 mg/cm^2 . The results showed that the addition of the DSO into the cathode catalyst layer can prevent cathode from flooding effectively at high current density and significantly improve the performance at room temperature. In order to further understand the polarization behaviors of the fuel cells with DSO loaded cathodes at elevated temperatures, the fuel cells with 0.5 mg/cm^2 DSO loaded cathode and normal cathode were tested at three different cell temperatures of 35°C , 50°C and 60°C under different cathode conditions. For the convenience of comparison, the operating conditions were the same as those done in Qi's group (Qi and Kaufman

2002). The conditions of cell temperature of 35°C, hydrogen inlet temperature of 45°C, and air inlet temperature at room temperature are denoted herein as 35/45/RT°C at an air stoichiometry of 2.1.

Fig. 5.11 and 5.12 show the effect of temperature on the performances of the fuel cells with normal cathode and 0.5mg/cm² DSO loaded cathode in the humidified Hydrogen and dry air. The fuel cell performances in the humidified air and humidified hydrogen at the same temperature range for both fuel cells are also demonstrated in Fig. 5.13 and 5.14. It can be found that the performances increased with the increase of the cell temperature for both fuel cells since temperature has a positive effect on the kinetics of the oxygen reduction reaction. The maximum power densities of the two fuel cells at different operating temperatures are summarized in Fig. 5.15. It was obvious that the performances for the fuel cell with 0.5mg/cm² DSO loaded cathode are much higher than those fuel cells with normal cathode at all temperatures in high current density region. When dry air was fed into the cathode as oxidant, the hydration of the electrolyte in the cathode side was dependent on the water produced by the electrochemical reaction. At high temperature such as 60°C, the flooding in the cathode was not significant so that the limiting current density for the fuel cell with normal cathode reached 77% of that of the fuel cell with DSO loaded cathode, e.g. 930 mA/cm² vs. 1200 mA/cm². But at lower temperatures such as 35°C and 50°C, the limiting current densities of the fuel cell with normal cathode only had 44% and 60% of those fuel cells with DSO loaded cathode, respectively.

Fig. 5.11 (a) Polarization V-I curves and (b) corresponding maximum power densities of the fuel cell with normal cathode at different temperatures in humidified hydrogen and dry air

Fig. 5.12 (a) Polarization V-I curves and (b) corresponding maximum power densities of the fuel cell with 0.5mg/cm² DSO loaded cathode at different temperatures in humidified hydrogen and dry air

Fig. 5.13 (a) Polarization V-I curves and (b) corresponding maximum power densities of the fuel cell with normal cathode at different temperatures in both humidified hydrogen and air

Fig. 5.14 (a) Polarization V-I curves and (b) corresponding maximum power densities of the fuel cell with 0.5mg/cm² DSO loaded cathode at different temperatures in both humidified hydrogen and air

Fig. 5.15 Maximum power density comparisons for cells with normal cathode and 0.5mg/cm² DSO loaded cathode at different temperatures

The results indicated that the fuel cell with normal cathode was easier to be flooded at lower cell temperature. Hence, the DSO loaded cathode showed more beneficial compared to the normal cathode in terms of resisting water flooding at lower temperature. When the fuel cells operated in the humidified air, the cathode was expected to be over-saturated with water. Furthermore, the oxygen partial pressure decreased in the humidified air because of the presence of water vapor. As a result, the performances of the fuel cell with normal cathode were much worse in the humidified air compared with the dry air in the high current density region for all three operating temperatures (Fig. 5.13). At 60°C, the maximum power density for the fuel cell with normal cathode only reached 296.7 mW/cm² in the humidified air, which was 100 mW/cm² lower than that in the dry air. Under this over-saturated condition, the DSO loaded cathode showed more advantageous in repelling water out

of the CCL than the normal cathode. As can be seen in Fig. 5.9 and 5.11, the performances of the fuel cell with DSO loaded cathode were only slightly lower than those in the dry air. The maximum power densities in the humidified air reached 430 mW/cm² at 50°C and 475 mW/cm² at 60°C, which were 19 mW/cm² and 67 mW/cm² lower than those in the dry air, respectively. Interestingly, the performance of the fuel cell with DSO loaded cathode was slightly improved from 385 mW/cm² in the dry air to 390 mW/cm² in the air humidified at 45°C (Fig. 5.15). This could be due to the relatively low saturation vapor pressure, which is only 0.096 bar at 45°C. Hence, the water in the anode may not be enough to facilitate good protonic conductivity when dry air was fed to the cathode.

5.3.3 Application of the DSO loaded cathode in a two-cell stack

The wide application of portable electronic devices is stimulating the rapid development of miniature power sources. Low cost self-breathing PEM fuel cell with light weight and high energy-conversion efficiency can meet such demand to some extent. However, due to the requirements for the intrinsic compact design, there are still several challenges remaining to be tackled (Kakaç *et al.* 2007). As oxygen from the air is fed by natural convection, the sluggishness of oxygen diffusion, heat and water management are the crucial issues encountered in the development of mini-micro PEM fuel cells. The cathode flooding has become a significant concern, since there is no forced air flow to remove the water droplets that are formed on the surface of the cathode. Furthermore, to increase the hydrogen utilization, dead end operation mode is desirable during the mini-micro fuel cell operation. However, this operation mode may exacerbate the electrode flooding and make the reactant starved which

fatally reduces the performance of a self-breathing PEM fuel cell. Encouraged by the promising results presented above, it is envisaged that the DSO loaded anti-flooding cathode would be attractive in the development of a self-breathing PEM fuel cell with improved water management.

Fig. 5.16 (a) Spiral/interdigitated channel design for anode and (b) circular opening design for cathode plate

A planar self-breathing fuel cell stack was designed and fabricated with Spiral/interdigitated channel in anode and circular opening design in cathode (Fig. 5.16). The spiral channel design not only has the advantages of traditional serpentine channel, but also can improve the current distribution. Furthermore, the fed hydrogen can be partly hydrated by the water near the outlet to achieve excellent results in dead-end mode (Chan *et al.* 2005). Interdigitated flow field design promotes forced convection of the fuel through the gas diffusion layer and facilitates water management and mass transport. Polymethylmethacrylate (PMMA) was chosen in this study as the fuel cell fixture because of its light weight and easiness for fabrication. In addition, this material offers other excellent properties such as low frictional coefficient, high chemical resistance and good electrical insulation. Thus, the flow

field for all of the cells in the stack can be connected in one PMMA plate to facilitate homogeneous fuel distribution as shown in Fig. 5.17. If graphite or metal were used as the fuel cell fixture in this study, this planar design would have to separate the anode plate and gas supply for each cell. Moreover, the transparent PMMA plate allows one to observe the in situ water accumulation in the anode and cathode flow field during fuel cell operation. The pictures of the assemble stack with view from the anode and cathode side are shown in Fig. 5.18.

Fig. 5.17 Design of two-cell stack

Fig. 5.18 Pictures of the assembled stack with view from the anode and cathode side

Fig. 5.19 Performance of the stack with 0.5mg/cm² DSO loaded cathodes in self-breathing and dead-end anode operation

Fig. 5.20 Impedance spectra of the fuel cell stack obtained at voltage of 1.5 V

Fig. 5.21 Stack performance with IR compensation for self-breathing under dead-end operation

Fig. 5.22 Long term stability of the fuel cell stack at voltage of 0.4 V with a small-axial fan over the self-breathing cathode

The stack using 0.5 mg/cm^2 DSO loaded cathodes was tested in the dry hydrogen with

dead-end at room temperature. The I-V polarization and power density curves are presented in Fig. 5.19. The limiting current was more than 1000 mA and the maximum power reached 450 mW. It was obvious from the polarization curve that the ohmic loss dominated the overall fuel cell performance, which was also confirmed by the impedance measurement. As shown in Fig. 5.20, the ohmic resistance of the stack was as high as 1.22 Ω . This high ohmic loss could be due to the poor contact between the MEA and the current collector made of the stainless steel mesh. The polarization curve with IR compensation under self-breathing is demonstrated in Fig. 5.21. It was found that the fuel cell performance could be improved by 10 times more if the ohmic loss was negligible. Thus, the future development should be focused on decreasing the ohmic resistance by using high conductivity current collector or improving the contact with the MEA. The long-term stability of the fuel cell stack at voltage of 0.4 V is demonstrated in Fig. 5.22 with a small-axial fan blowing air over self-breathing cathode. The current can stably maintain at around 700 mA for 20 hours. The stack performance was slightly increased after 20 hrs of operation, which could be attributed to the gradual hydration of the membrane by the back diffusion of water from cathode to anode. This speculation was confirmed by observing some amount of small water droplets in channel of the dead-end anode after 20 hrs of operation. In literature, it has been experimentally and numerically demonstrated that neither the natural-evaporation mechanism nor force convection at the cathode opening can effectively remove water out of the cathode (Bussayajarn *et al.*, 2009). Thus, the improved water management of the DSO-loaded cathode is believed to be the main factor causing the excellent performance of the self-breathing PEM stack.

Chapter 6. Effect of cathode structure on water management of PEM fuel cell

6.1 Introduction

One of the important components in the PEM fuel cells is the porous gas diffusion layer (GDL), which conducts electrons between the catalyst layer and the current collector and transports reactants and products to and from the catalyst layer. The GDL in the cathode is of particular importance in controlling water management to avoid flooding and membrane dehydration. The properties of the cathode GDL, such as porosity, pore size distribution and hydrophobicity, have been found to be critical for the efficient water management. In literature, there are two GDL configurations that have been commonly studied; i.e. single layer GDL and dual-layer GDL. The single layer GDL is a sheet of electrically conductive macro-porous substrate (MaPS), such as a non-woven carbon paper or a woven carbon cloth typically wet-proofed with a polytetrafluoroethylene (PTFE) coating. The single-layer GDL has macro-pores in its structure, allowing the effective transport of gas reactants to the catalyst layer. However, it gives rise to large contact resistance with the catalyst layer and poor physical support to the catalyst particles. Furthermore, this configuration was reported to be unfavourable to water management in the fuel cell (Park *et al.* 2004).

The dual-layer GDL is named because a thin micro-porous layer (MPL) of carbon black mixed with PTFE is placed between catalyst layer and conventional MaPS. The MPL can provide good physical support for the catalyst layer and minimize the

electrical contact resistance (Weber and Newman 2005). In addition, the MPL has been known to play a key role in effectively removing water product from the cathode. The coarse pore structure of backing layer allows for growth of large liquid water droplet, but the hydrophobic fine pore structure in MPL can limit their growth and prevent the stable droplet forming (Wilson *et al.* 1995; Qi and Kaufman 2002). It was also reported that the MPL could create a pressure barrier for the water product at the catalyst layer to keep the membrane better hydrated (Spernjak *et al.* 2007). However, the introduction of MPL in the GDL will increase the cathode thickness and tortuosity, thereby increasing the difficulty of the gas transport within the cathode. As a result, the dual-layer GDL would confront with a large mass transport limitation than the single-layer GDL at a higher current density (Han *et al.* 2008).

In the previous Chapters, the effects of the hydrophobicity of the cathode catalyst layer on the performance of the PEM fuel cell with single-layer GDL in cathode have been investigated. To further understand the role of the cathode structure on the water management, in this study, the effects of MPL coupled with different cathode catalyst layers on the fuel cell performance are investigated. The physical properties and electrochemical behaviors of fuel cells with four different cathode, e.g. normal CCL without MPL, normal CCL on MPL, DSO loaded CCL without MPL and DSO loaded CCL on MPL, are compared and discussed to understand the mechanism of the water management in the cathode using various characterization techniques such as SEM, porosimetry analysis, electrochemical impedance spectrometry analysis and steady-state polarization.

6.2 Experimental

The carbon paper TGP-H-090 was used as electrode backing layer. The PTFE-treated carbon papers were directly applied as the single-layer GDL and the backing layer of the dual-layer GDL. The MPL applied on the teflonated backing layer was prepared similar to that reported by Han *et al.* (Han *et al.* 2008). The loading of carbon (Vulcan-72) was ca. 1 mg/cm^2 and the PTFE content was around 33% in the MPL. The carbon-supported 50 wt. % Pt/C (Johnson Matthey) and 5% Nafion solution were employed to make the catalyst layer. An appropriate amount of DSO (Shin-Etsu, Japan) was emulsified into a mixture of catalyst and Nafion by a highly intensive ultrasonic machine (Vcx 750, Sonics, USA) to make the DSO loaded cathode electrode. The resulting amounts of Pt and Nafion loadings in CL were 0.35 mg/cm^2 and 0.56 mg/cm^2 in all the electrodes. For the DSO loaded cathode catalyst layer, the content of DSO is 0.5 mg/cm^2 . A commercial Nafion 112 membrane (EW 1100, Dupont) was employed in the membrane electrode assembly (MEA). Hydrogen and air were fed into the anode and cathode, respectively, at a constant flow rate with stoichiometry of 2.1 calculated at 1 A/cm^2 .

6.3 Results and discussion

6.3.1 SEM observation

In the three layer structure cathode, a MPL was sandwiched by the macro porous substrate (MaPS) and catalyst layer (CL). TGP-H-090 carbon paper was used as the MaPS with thickness about 0.28 mm. As can be seen in Fig. 6.1, the MPL consisting of carbon/PTFE mixture (33 wt% PTFE and 1 mg/cm^2 Vulcan-72 carbon

loading) has a uniform thickness around 50 μm . A clean boundary between the two layers is observed which means that there is no tremendous intrusion of carbon/PTFE mixture into the MaPS. As shown in the magnified SEM image, the MPL layer shows a homogeneous and porous surface with small agglomerates of carbon powder and PTFE, which was also observed by other researchers (Giorgi *et al.* 1998). Compared with surface of MaPS (shown in Fig. 4.1), this MPL structure has finer pore and uniform pore size distribution, which is believed to provide a better contact and support for the catalyst and facilitate the water removal. Fig. 6.2 shows the top-views of the normal CCL and the CCL loaded with 0.5 mg/cm^2 DSO. They are significant difference in the pore size and the shape of the pores. The majority pores on the surface of the DSO-loaded CCL are in circular shape. However, the pore shape on the normal CCL is irregular. Apparently, the normal CCL presents higher compactness and fewer large crackers due to the smaller pore size, most of which is less than 0.5 μm . While for the CCL loaded with 0.5 mg/cm^2 DSO, most of the pore sizes are in the range of 0.5-3 μm .

Fig. 6.1 SEM image of the cross-section of the cathode with micro porous layer (MPL) between the macro porous substrate (MaPS) and the catalyst layer (CL)

Fig. 6.2 Top-views of the CCL for the normal CCL (a) and the DSO-loaded CCL (b) with MPL between the MaPS and the CCL

6.3.2 Pore size distribution analysis

The cumulative pore volume and pore size distribution significantly changed with varying the GDL structure, indicating the effect of the cathode structure on the porous system of the GDL. In the presence of MPL between the MaPS and the CCL, the porosity and pore size distribution of the cathode are quite different from the cathodes without MPL as shown in Fig. 4.8. Fig. 6.3 (a) presents the cumulative pore volume vs. pore size for the normal cathode and the cathode loaded with 0.5 mg/cm^2 DSO obtained from the mercury intrusion data. For the both cathodes, the sharp increase of the cumulative pore volume from $0.2 \text{ cm}^3/\text{g}$ to $1.1 \text{ cm}^3/\text{g}$ in the pore diameter range from $10 \text{ }\mu\text{m}$ to $100 \text{ }\mu\text{m}$ illustrated that most of the pores are located in macro-porous carbon paper substrate. The differential pore volume ($dV/d\log d_p$) for the normal cathode and the cathode loaded with 0.5 mg/cm^2 DSO is demonstrated in Fig 6.3 (b). Two obvious peaks can be observed. The high peak in pore size range from $10 \text{ }\mu\text{m}$ to $100 \text{ }\mu\text{m}$ is from the carbon paper substrate. It was found that the amount of pores located in size $10 \text{ }\mu\text{m}$ to $100 \text{ }\mu\text{m}$ decrease significantly when the MPL is present (Fig.

4.8b and Fig. 6.3b). This indicates that part of carbon particles in the MPL has entrenched into the carbon fiber substrate during the spread of carbon ink.

The small peak in pore size range from 0.02 μm to 0.5 μm is contributed by the MPL. Since the MPL is composed of carbon black (Vulcan XC-72) and PTFE, the macropore size is primarily determined by the size of carbon particle aggregates. For Vulcan XC-72, the primary particle size is about 5-10 nm. These primary particles form aggregates of micron size as illustrated in the pore size distribution curve. Water may not be able to form stable droplets inside such small and hydrophobic pores (Qi and Kaufman 2002). Therefore, the permeability of liquid water could be reduced by MPL, which results in a higher liquid water pressure profile within MPL to push more water back to the anode through the membrane (Lin and Van Nguyen 2005). The fluctuation of the differential volume in the DSO loaded cathode suggests that the addition of DSO in the CCL could create more random size pores in the range of 0.004 μm to 5 μm . This random size pores created by the addition of DSO are occupied by the liquid DSO in the actual operation of the PEM fuel cell. With the similar function as the MPL, the hydrophobicity created by the DSO in the CCL can significantly increase the capability of repelling water out of the CCL.

Fig. 6.3 (a) The cumulative volume and (b) pore size distribution for the normal cathode with MPL and the cathode loaded with 0.5 mg/cm² DSO with MPL

6.3.3 Fuel cell performance

(1) The role of the MPL in water management

It is well known that MPL has a dramatic effect on the water management of PEM fuel cell. However, from the experimental data, it has been concluded that such improvements are dependent on the fuel cell system and operating condition. To better understand the role of MPL in the PEM fuel cell cathode, the electrochemical performances of the fuel cells with three different cathodes, e.g. normal CCL without MPL, normal CCL on MPL, and DSO loaded CCL without MPL, will be investigated under two different humidification conditions: humidified H₂/dry air and dry H₂/dry air. The IV curves of the three fuel cells tested in humidified H₂ and dry air were recorded and shown in Fig. 6.4. Under this condition, the humidified H₂ in the anode can hydrate the membrane to facilitate the proton transport. Meanwhile, in the cathode side, the dry air could take away the water generated by ORR and that migrated from anode to cathode by electro-osmotic drag, thus reducing the possibility of liquid water retention in the cathode. Compared to the fuel cell with normal cathode, significant performance improvements were observed for the fuel cells with normal CCL with MPL, and DSO loaded CCL without MPL. The limiting current density of the fuel cell with normal CCL with MPL reached 900 mA/cm² which is more than two times higher than that of the fuel cell with normal CCL without MPL of 400 mA/cm². However, the performance of the fuel cell with DSO loaded CCL without MPL is comparable with that of the fuel cell with normal CCL with MPL. The fuel cell with DSO loaded CCL without MPL was found to have slightly poorer performance at low current density, but it succeeded the fuel cell with normal CCL with MPL at high current density. More specifically, at voltage of 0.6 V, the current

densities were 516 and 391 mA/cm² for the fuel cell with normal CCL on MPL cathode and DSO loaded CCL without MPL, respectively. At voltages lower than 0.4 V, higher current densities were observed for the fuel cell with DSO loaded CCL without MPL than that of the fuel cell with normal CCL on MPL.

Fig. 6.4 Comparisons of first I-V curves for fuel cells with normal CCL on both MPL and MaPS and DSO loaded CCL on top of MaPS using humidified H₂ and dry air at room temperature

In order to fundamentally understand the structure-related performance difference, electrochemical impedance spectroscopy (EIS) has been carried out to identify the physical and electrochemical factors that may affect the fuel cell water management and performance. Fig. 6.5 exhibits the impedance spectra obtained at various cell voltages for the fuel cells with three different types of cathodes. The EIS data were fitted to the equivalent circuit with elements of $R_1(R_2CPE1)(R_3CPE2)$ as in Fig. 4.11.

Fig. 6.5 (a) Impedance spectra obtained at various values of cell voltages for fuel cell with (a) normal CCL on MPL (b) normal CCL on MaPS and (c) DSO loaded CCL on MaPS as cathode using humidified H₂ as fuel and dry air as oxidant

Fig. 6.6 (a) The total ohmic resistance and (b) the effective charge transfer resistance vs. voltages for three fuel cells with different types of cathodes

Fig. 6.6 (a) summarizes the total ohmic resistance of the fuel cells with three different types of cathodes as a function of cell voltage. At low cell voltage (e.g. high current

density), similar total ohmic resistances for all three fuel cells were observed due to the good hydration of the membrane by the generated water. However, at high voltage such as 0.8 V, because of low output current, the generated water is not sufficient to fully hydrate the electrolyte. As a result, higher total ohmic resistances were expected at higher cell voltages. Among the three fuel cells, the fuel cell with normal CCL on MPL shows the lowest total ohmic resistance, confirming the function of MPL to create a pressure barrier to push the generated water to the membrane (Lin *et al.* 2004; Weber and Newman 2005). While, the fuel cell with DSO loaded CCL without MPL has much higher ohmic resistance than the other two fuel cells. This could be due to the low level of water retention in the catalyst layer induced by the higher hydrophobicity of DSO, leading to the low proton conductivity in the catalyst layer and membrane.

Fig. 6.6 (b) illustrates the effective charge transfer resistance at each voltage for the all three fuel cells with different types of cathodes. It is obvious from the results that the charge transfer resistance decreases in the order of $R_{\text{DSO no MPL}} > R_{\text{normal no MPL}} > R_{\text{normal with MPL}}$ at cell voltage of 0.8 V. However, at voltages less than 0.6 V, the order of the charge transfer resistance changes to $R_{\text{normal no MPL}} > R_{\text{normal with MPL}} > R_{\text{DSO no MPL}}$. As discussed in Chapter 4, the effective charge transfer resistance is associated with the rate of the interfacial oxygen reduction process, the protonic conductivity and the oxygen permeability limitations within the CCL. At cell voltage of 0.8 V, the low level of water retention in the DSO loaded CCL limits the protonic conductivity, which impedes the oxygen reduction. With the decrease of the cell voltages, the water level in the CCL increases significantly. As a result, at cell voltage of 0.4 V, the fuel cell with normal CCL without MPL begins to be controlled by the oxygen mass

transport due to the flooded CCL. In addition, even though flooding phenomena were not observed for the fuel cells with normal CCL on MPL and DSO-loaded CCL without MPL at high current densities (e.g. low cell voltages), the mass transport resistances of the fuel cell with normal CCL on MPL were found to be higher than those of the fuel cell with DSO loaded CCL without MPL, which could be due to the additional diffusion resistance of oxygen through MPL (Lim and Wang 2004).

It has been well known that the presence of MPL can significantly improve the performance of a PEM fuel cell by preventing the water flooding within the cathode. The major factor for the improved water management is believed to be the micro-porosity in MPL, which may prevent the formation of stable water droplet in the hydrophobic micron size pores inside MPL. However, it is still under debating whether MPL helps to reduce water saturation in the adjacent CCL by providing wicking of liquid water to MaPS (Qi and Kaufman 2002; Lim and Wang 2004) or to increase the membrane hydration by enhancing back-diffusion of water from the cathode to anode (Lin and Van Nguyen 2005; Weber and Newman 2005; Karan *et al.* 2007). To further understand the mechanism by which the MPL improves the fuel cell performance, the polarization curves of the fuel cells with three types of cathodes in dry H₂/dry air were obtained and compared in Fig. 6.7. For the fuel cell with normal CCL without MPL, the dehydration of membrane fatally affected the fuel cell performance. For the fuel cell with normal CCL on MPL, the current dropped quickly at the beginning of the IV sweep due to the low conductivity of the electrolyte. However, when the cell voltage reached 0.6 V, there was an obvious increase in the current density. Similar behavior was also observed in the IV curve of the fuel cell with DSO loaded CCL without MPL. This phenomenon could be explained by the

electrolyte hydration due to the retention of the generated water within the cathode, significantly decreasing ohmic resistance of the electrolyte.

Fig. 6.7 Comparisons of I-V curves for the fuel cells with normal CCL on both MPL and MaPS and DSO loaded CCL on MaPS in dry H₂/dry air at room temperature

The low liquid water permeability of the MPL impedes the transport of liquid water from CCL to the MaPS while forcing more water back to the anode. This was reported to result in a lower liquid saturation level in the macro-porous layer and higher gas transport rate from the channel to the CCL (Lin and Van Nguyen 2005). Since the pore size in CCL is in the same magnitude as the pores in the MPL, the hydrophobic CCL modulated by DSO can function as a watershed similar to the MPL. Therefore, the liquid water generated in the DSO-loaded CCL could be broken up significantly and pushed back to the membrane. Furthermore, the MPL imposes an additional diffusion resistance to the oxygen transport into the catalyst layer (Lim and Wang 2004). As a result, at the high current density region, the performance of the

fuel cell with DSO loaded CCL without MPL is even better than that of the fuel cell with normal CCL on MPL.

(2) Effect of CCL hydrophobicity on the fuel cell performance in the presence of MPL

In this section, the effect of CCL hydrophobicity on the performance of the PEM fuel cell with MPL in the cathode GDL was explored under various operation conditions. Polarization curves for both normal CCL and DSO loaded CCL on MPL were obtained and demonstrated in Fig. 6.8 with humidified H₂ as fuel and dry air as oxidant at room temperature. A slight improvement was observed for the fuel cell with DSO loaded CCL on MPL at the high current density zone. In view of the fact that MPL in the cathode side is intended to provide wicking of liquid water into the MaPS or back into the catalyst layer, the increased hydrophobicity of CCL could benefit water drainage from CCL into the MaPS and then out of cathode at high current density. With the combined effect of the MPL and the hydrophobic CCL, the fuel cell with DSO-loaded CCL on MPL is expected to have higher limiting current density due to its higher ability to prevent cathode flooding. This conclusion is also supported by the long-term stability test at a constant voltage of 0.4 V operated using humidified H₂ and dry air at room temperature (shown in Fig. 6.9). It is not surprised to see that the fuel cell with DSO loaded CCL on MPL has a higher output current density.

Fig. 6.8 I-V curves for the fuel cells with normal CCL and DSO loaded CCL on MPL in humidified H₂ and dry air at room temperature

Fig. 6.9 Long-term stability of the fuel cells with different types of cathodes operated at a constant voltage of 0.4 V in humidified H₂ and dry air at room temperature

Both fuel cells were further tested under no humidification at room temperature to understand the water retention ability within the cathode. As shown in Fig. 6.10, the performance of the fuel cell with DSO loaded CCL on MPL dropped significantly at the beginning of the IV sweep, but recovered back to normal at high current density. This phenomenon could be due to the poor water retention ability of the cathode with DSO-loaded CCL on MPL caused by the over repelling of water out of the CCL. Based on the experimental data obtained, one should bear in mind that the hydrophobic level of the CCL is critical and must be carefully controlled to balance the conflicting requirements of the electrolyte hydration and the cathode anti-flooding. Fig. 6.11 presents the EIS patterns for both fuel cells with normal CCL and DSO loaded CCL on MPL. It was found that the charge transfer resistance of the fuel cell with DSO loaded CCL on MPL is much smaller than that of the fuel cell with normal CCL on MPL. According to the analysis in Chapter 4, at cell voltage of 0.5 V, the water in thin film diffusion has dominated the oxygen transfer in the CCL. Since the solubility of oxygen in DSO is almost 10 times higher than that in water at room temperature, the occupation of DSO within the CCL pores can facilitate the oxygen transport to the reaction sites (Ji *et al.* 2009), leading to a reduced charge transfer resistance.

Fig. 6.10 I-V curves for the fuel cells with normal CCL and DSO loaded CCL on MPL in dry H₂ and dry air at room temperature

Fig. 6.11 EIS obtained at voltage of 0.5 V for the fuel cells with normal CCL and DSO loaded CCL on MPL in humidified H₂ and dry air at room temperature

(3) Analysis of polarization curves to investigate the oxygen transport in cathode

In this section, in order to understand the oxygen transport in the cathode, the method proposed by Williams *et al.* was adopted to analyze the polarization curves previously shown in Fig. 6.4 (Williams *et al.* 2005). The results were used to determine the overpotential resulting from different physical and electrochemical processes in the PEM fuel cell. Two assumptions should be made before the analysis of the polarization curves: (i) a first order of ORR with respect to oxygen concentration follows the Butler-Volmer equation kinetics; and (ii) the anode polarization is negligible. The later assumption is valid since the exchange current density for the hydrogen oxidation reaction has several orders of magnitude higher than that of the sluggish ORR. Furthermore, pure hydrogen is provided in anode and hydrogen has a much smaller molecule than oxygen, resulting in less hydrogen concentration polarization. Hence, the concentration polarization can be considered to be the only caused for the oxygen transport in the cathodic GDL and CCL. The total polarization of a PEM fuel cell includes losses originated primarily from the following three sources: activation overpotential (η_{act}), ohmic overpotential (η_{ohm}), and concentration overpotential (η_{conc}). The actual cell voltage can be written as:

$$E_{cell} = E_{eq} - \eta_{act} - \eta_{ohm} - \eta_{conc} \quad (6-1)$$

Where E_{cell} is the experimental cell voltage in a polarization curve, E_{eq} the theoretical equilibrium cell voltage.

The theoretical equilibrium cell voltage can be calculated by the equation below (Bernardi and Verbrugge 1992; Zhang *et al.* 2006):

$$E_{eq} = 1.229 - 0.000846(T - 298.15) + 2.303 \frac{RT}{4F} (P_{H_2}^2 P_{O_2}) \quad (6-2)$$

where R is the universal gas constant, T the temperature in Kelvin, and F the Faraday constant. p_{O_2} and p_{H_2} the partial pressures (atm) of O_2 and H_2 , respectively. At room temperature the E_{eq} is 1.23V.

The measured cell potential E_{cell} in Fig. 6.4 was firstly compensated with total ohmic losses as followed:

$$E_{iR-corrected} = E_{cell} + \eta_{ohm} \quad (6-3)$$

The corrected polarization curves are presented in Fig. 6.12 for the fuel cells with different cathodes. To determine the oxygen transport resistance through layers where oxygen is not consumed, the limiting current density i_{lim} needs to be evaluated. The theoretical basis for evaluating the limiting current is based on a first order oxygen reduction, the Butler-Volmer equation kinetics and the limiting current condition of zero oxygen concentration at the catalyst surface. Hence, the Tafel equation was modified as follows (Williams *et al.* 2005):

$$i_{kin} = \frac{i}{1 - i/i_{lim}} = i'_0 \exp \frac{\eta_{iR-corrected}}{b_{cor}} \quad (6-4)$$

where i_{lim} is the limiting current density, i_{kin} the kinetic current density corrected for i_{lim} , $\eta_{iR-corrected}$ the iR-corrected overpotential, and b_{cor} the empirical Tafel slope in high current density which characterizes the oxygen reduction kinetics in the absence of oxygen transport limitation in the catalyst layer (deLevie 1967). b_{cor} is different from the kinetic Tafel slope b_k at low current density. The corrected value of i_{lim} was determined by an iterative procedure based on Eq. (6-4) until the plot of $E_{iR-corrected}$ vs. $\log i_{kin}$ became a straight line in the high current density region. The reconstructed iR-corrected and limiting current eliminated polarization curves for fuel cell with DSO

loaded CCL on MaPS was demonstrated in Fig. 6.13. The value of limiting current used to calculate i_{kin} was found to be 938 mA/cm². The value of b_{cor} according to the slope of the straight line on the semilog plot at the zone with $i_{kin} > 1000$ mA/cm² was 99 mV/dec. The kinetic Tafel slope b_k was 58 mV/dec which was fitted to the iR -corrected polarization curve in the range of around 10 mA/cm² to 100 mA/cm² in which oxygen reduction is mainly controlled by the activation polarization.

Fig. 6.12 Polarization curves corrected for the total ohmic losses for fuel cells with normal CCL on both MPL and MaPS and DSO loaded CCL on MaPS in humidified H₂ and dry air at room temperature

The values of b_{cor} and kinetic Tafel slope b_k for the fuel cells with normal CCL on MPL and MaPS were fitted in same manner and summarized in Fig. 6.14. It was found that the values of b_{cor} was approximately two times higher than the kinetic Tafel slope b_k , indicating that the oxygen transport limitation in catalyst layer significantly affected the fuel cell polarization in the intermediate current range. It has been experimentally confirmed that the second Tafel slope is controlled by the oxygen

diffusion in the agglomerate of the CCL (Ihonen *et al.* 2002). The effect of oxygen transport kinetics in the CCL on the fuel cell polarization was simulated and shown that the slope of the Tafel plot in the intermediate current range is two times larger than the kinetic Tafel slope measured in the activation region (Springer and Raistrick 1989; Raistrick 1990; Jaouen *et al.* 2002). It was obvious that the value of b_{cor} for the fuel cell with normal CCL without MPL is much higher than that for the other two fuel cells. It means that the fuel cell with normal CCL without MPL has the highest oxygen transport resistance in the CCL, indicating the serious flooding in its CCL. The value of b_{cor} for the fuel cell with normal CCL on MPL is almost the same as that for the fuel cell with DSO loaded CCL without MPL. In summary, both cathodes with normal CCL on MPL and with hydrophobic CCL on MaPS could effectively reduce the water saturation and increase the oxygen transport in the CCL. The improved water management can be attributed to the hydrophobic micro-pore structure in the CCL and MPL, which provides wicking of liquid water to MaPS and enhances back-diffusion of water to the membrane.

Fig. 6.13 IR-corrected polarization curves of the PEM fuel cell with DSO loaded CCL on MaPS presented in terms of the measured current density and the kinetic current density i_{kin}

Fig. 6.14 The kinetic Tafel slope b_k and the empirical Tafel slope b_{cor} for the three fuel cells with normal CCL on both MPL and MaPS and DSO loaded CCL on MaPS

Chapter 7. Mathematic analysis of water transport within the CCL of PEM fuel cell

7.1 Introduction

High current density output in PEM fuel cell is of particular interests for the vehicle applications. Due to the generation of excessive water at cathode under high current density, two-phase transport of oxygen and liquid water within the cathode dominates the fuel cell performance. The cathode flooding happens when liquid water occupies the open pores of CCL and GDL and block the transport of oxygen from bulk to the reaction sites. Water may cover the Pt catalyst particles thus hinders the electrochemical reaction. The flooding phenomenon is dependent on a number of factors, such as microstructure of the cathode, operating conditions, materials properties, and so on. Experimental approach to optimize the cathode is costly and time-consuming. Modelling analysis of the two-phase transport within the cathode can provide fundamental understanding of the parametric effects so as to guide the design of high performance fuel cells.

Many efforts have been put to develop water-transport models for the prediction of PEM fuel cell performance (He *et al.* 2003; Nam and Kaviani 2003; Wang 2004; Eikerling 2006; Gostick *et al.* 2006; Falcao *et al.* 2009), especially the two-phase transport model (You and Liu 2002; Pasaogullari and Wang 2005; Jiao and Zhou 2008; Meng 2009; Park and Popov 2009). Due to the complicated processes within the CCL, most of the models focused on the water transport through the membrane, the GDL, or

the gas flow channel. The CCL was treated as an infinite layer so that the water was assumed to be produced at the CCL/GDL interface (Pasaogullari and Wang 2004; Park and Popov 2009). However, the highest current density was found to be generated at the CCL/membrane interface (Eikerling and Kornyshev 1998). In addition, the experimental results in Chapter 4, 5 and 6 showed that the cathode flooding could be significantly prevented by changing the hydrophobicity of the CCL even though the same GDL was used. Therefore, understanding of the water transport within the CCL is importance both for practical development and fundamental understanding.

The objective of this Chapter is to develop a mathematic model, which considers the interdependency among the electrochemical reaction, water transport, and oxygen transport within the CCL. Pasaogullari and Wang (2004) developed a set of analytical equations to investigate the two-phase transport in hydrophobic GDL. By combining their analytical equations with the CCL model developed here, the water generation with the CCL and the expelling of water from CCL to gas flow channel through the GDL are simulated in one-dimensional manner. The simulation model developed is to understand the effects of hydrophobicity of the CCL on the water flooding of the cathode and the performance of PEM fuel cell.

7.2 Mathematic model for two-phase flow and transport in CCL of the PEM fuel cells

The overall electrochemical reaction occurring in the PEM fuel cell can be written as:

During the fuel cell operation, the cathode dominates the fuel cell performance due to the following three factors: (i) The kinetics of the oxygen reduction is much more sluggish than that of the hydrogen oxidation; (ii) The oxygen diffusion is slower than the hydrogen diffusion; and (iii) The liquid water is produced in the cathode side during the fuel cell operation, which may cause flooding in the fuel cell. Thus, understanding of the liquid water and oxygen transport in cathode is practically important for the design of high performance fuel cell.

7.2.1 Model description of the CCL

The fuel cell catalyst layer is where the electrochemical reactions occur. Inside the catalyst layer, Pt catalyst offers favourable reaction sites for the electrochemical reaction; carbon black acts as Pt catalyst support and transports electron between the current conductor and the active reaction sites; and Nafion electrolyte transports proton between the Nafion membrane and the active reaction sites. Due to the fast mass transport of H_2 and rapid electrochemical kinetics of the H_2 electro-oxidation, the polarizations of the anode under fuel cell operation are negligible compared to those of the cathode. Thus, in the following sections, only losses in cathode side are considered and expressed as in concentration and activation polarizations as shown in Eq. (7-1). The schematic diagram and the corresponding equivalent circuit of the mass transport and ionic and electronic transport within the cathode catalyst layer are illustrated in Fig. 7.1 and 7-2, respectively. The focus of this section is to develop a reaction model for the CCL to predict/model the effect of microstructure, electrode properties, water flooding, and operating conditions on the cathode performance.

Fig. 7.1 schematic of a PEM fuel cell

Fig. 7.2 Equivalent circuit of porous CCL

Several assumptions should be made before establishing the conservation of mass, momentum and charge within the CCL, e.g. (i) the fuel cell in operating under steady state condition and the membrane is fully humidified so that the active surface area and ionic/electronic resistivity are uniform throughout the CCL; (ii) pressure is constant within the CCL; (iii) only hydrophobic GDL is considered in this study; (iv) the electrochemical reactions at membrane/CCL interface and CCL/GDL interface are negligible; (v) only one-dimension of the CCL is considered in this case; (vi) the

oxygen transport in the liquid water is negligible compared to the gas phase. Since water transport from anode to cathode through electro-osmotic drag is somehow setoff with the back-diffusion water from cathode to anode. Hence, only the water generated through ORR is considered in this model.

Under the above assumptions, the Ohm's law and charge balance within the reaction zone $[x, x+dx]$ of the CCL are listed as follows:

Ohm's law based on the equivalent circuit in Fig. 7.2:

$$\frac{d\phi_{\text{prot}}}{dx} = -i_{\text{prot}} \rho_{\text{prot}}^{\text{eff}} \quad (7-2a)$$

$$\frac{d\phi_{\text{el}}}{dx} = -i_{\text{el}} \rho_{\text{el}}^{\text{eff}} \quad (7-2b)$$

Charge balance

$$\frac{di_{\text{el}}}{dx} = -\frac{di_{\text{prot}}}{dx} = A_v i \quad (7-2c)$$

Where i is the local current density generated by electrochemical reaction at position of x , which is given by the Butler Volmer equation:

$$i = i_{\text{O}_2}^0 \frac{C_{\text{O}_2}}{C_{\text{O}_2}^0} \left\{ \exp\left[\frac{(1-\alpha)nF}{RT}\eta_c\right] - \exp\left[-\frac{\alpha nF}{RT}\eta_c\right] \right\} \quad (7-3)$$

where $i_{\text{O}_2}^0$ is the exchange current density for oxygen reduction reaction, C_{O_2} and $C_{\text{O}_2}^0$ are the actual oxygen concentration at the reaction site and reference oxygen concentration, respectively. n is the number of electrons transferred in the electrochemical reaction, and η_c is the cathode activation overpotential, which is the driving force for the electrochemical reaction. In the CCL, the electrical resistivity is several orders lower than the protonic resistivity. Thus, combining Eq. 7-2 with overpotential defining as $\eta_c = \phi_{\text{el}} - \phi_{\text{prot}}$, one can get

$$\begin{aligned}\frac{d^2\eta_c}{dx^2} &= (\rho_{\text{prot}}^{\text{eff}} + \rho_{\text{el}}^{\text{eff}}) A_v i \\ &\approx \rho_{\text{prot}}^{\text{eff}} A_v i\end{aligned}\quad (7-4)$$

The conservation equation for the oxygen can be written as:

$$4F \frac{dJ_{\text{O}_2}}{dx} = 4FD_{\text{O}_2}^{\text{eff}} \frac{d^2C_{\text{O}_2}}{dx^2} = A_v i \quad (7-5)$$

$$\frac{d^2C_{\text{O}_2}}{dx^2} = \frac{A_v i}{4FD_{\text{O}_2}^{\text{eff}}} \quad (7-6)$$

where J_{O_2} is the diffusion of oxygen, and $D_{\text{O}_2}^{\text{eff}}$ is the effective diffusion coefficient of oxygen.

Water is produced within the CCL during the electrochemical reaction. Thus, oxygen gas, water vapour and liquid water coexist within the CCL. Assuming that the electrochemically water product is in liquid phase, the conservation of the liquid water within the reaction zone $[x, x+dx]$ of the CCL can be expressed as:

$$\varepsilon_l \rho_l \frac{du_l}{dx} = K_{g-l} (\chi_g^{\text{H}_2\text{O}} p_g - p_{\text{sat}}) + M_{\text{H}_2\text{O}} A_v \frac{i}{2F} \quad (7-7)$$

The first term in the right side of the equation represents the condensation/vaporization of the water and the second term represents the production of liquid water from the electrochemical reaction. Because the water vapour is fully saturated in the gas phase within the CCL under steady state condition, the water condensation/vaporization can be neglected in the CCL.

The driving force for the liquid water transportation within the CCL is the liquid pressure gradient according to the Darcy's law. Thus, the conservation of momentum for the liquid water under the steady state condition can be written as:

$$\varepsilon_l \frac{dp_l}{dx} = \frac{\varepsilon_l \mu_l}{Kk_{rl}} u_l \quad (7-8)$$

where μ_l is the liquid water viscosity; u_l is the phase averaged velocity; K is the absolute permeability; k_{rl} denotes the relative permeability of the liquid phase in the CCL, and ε_l is the pore volume fraction occupied by liquid water. Within the CCL, the capillary pressure, P_C , is the difference between the gas and liquid phase pressure, e.g. $p_C = p_g - p_l$. With this relation and the assumption that the gas pressure is constant throughout the CCL and GDL, Eq. (7-8) can be re-written as:

$$\frac{dp_C}{dx} = -\frac{\mu_l}{Kk_{rl}}u_l \quad (7-9)$$

7.2.2 Parameters of the model

Liquid saturation

Liquid saturation, s , is defined as the fraction of the liquid volume in the total void volume of porous electrode (Pasaogullari and Wang 2004):

$$s = \frac{V_l}{V_{total}} = \frac{\varepsilon_l}{\varepsilon} \quad (7-10)$$

Specific active surface area

The specific active surface area can be estimated from the catalyst mass loading (m_{Pt}), catalyst surface area per unit mass of catalyst (A_s), and the thickness of CCL (L_C),

$$A_v^* = \frac{A_s m_{Pt}}{L_C} \quad (7-11)$$

Considering the reduction of the active surface area due to the liquid water coverage on the catalyst particles, the specific active surface area can be corrected by a factor of $(1-s)$ to be the local specific active surface area:

$$A_v = (1-s)A_v^* = (1-s) \frac{A_s m_{Pt}}{L_c} \quad (7-12)$$

Exchange current density

An empirical equation is adopted to estimate the exchange current density (unit of A/cm²) of oxygen reduction in Nafion as a function of temperature (Parthasarathy *et al.* 1992).

$$\log_{10}(i_{O_2}^0) = 3.507 - \frac{4001}{T} \quad (7-13)$$

Relative permeability

The relative permeability is defined as the ratio of intrinsic permeability of a phase (liquid water or water vapour) at a given saturation to the total intrinsic permeability of a porous CCL. The cubic relation between the relative permeability of liquid water and liquid water saturation is widely used to estimate the relative permeability.

$$k_{rl} = s^3 \quad (7-14)$$

Capillary pressure

The capillary pressure between gas and liquid phase within a porous CCL can be empirically expressed as (Kaviany 1991):

$$p_c = \sigma \cos \theta_c \left(\frac{\varepsilon}{K} \right)^{0.5} F(s) \quad (7-15)$$

Where $F(s)$ is the Leverette function with the following relation:

$$F(s) = \begin{cases} 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3 & \text{if } \theta_c < 90^\circ \\ 1.417s - 2.120s^2 + 1.263s^3 & \text{if } \theta_c > 90^\circ \end{cases} \quad (7-16)$$

σ is surface tension of liquid water, which is 0.0625 N/m^2 for liquid water-air system.

θ_C is the contact angle of liquid water on the solid surface. Since cathode catalyst layer consists of hydrophilic materials (Nafion, carbon) and hydrophobic agent (DSO), the contact angle for composite structure can be defined as: (Weber *et al.* 2004; Park and Popov 2009)

$$\theta_C = \cos^{-1}[f_{HI} \cos\theta_{HI} + (1 - f_{HI}) \cos\theta_{HO}] \quad (7-17)$$

where f_{HI} is the hydrophilic fraction of the cathode catalyst layer. θ_{HI} and θ_{HO} denote the hydrophilic contact angle and hydrophobic contact angle, respectively.

Effective oxygen diffusion coefficient

$$D_{O_2} = \frac{1 - X_{O_2}}{\frac{X_{N_2}}{D_{O_2-N_2}} + \frac{X_{H_2O}}{D_{O_2-H_2O}}} \quad (7-18)$$

Where X_{O_2} , X_{N_2} and X_{H_2O} are the mole fractions of oxygen, nitrogen, and water vapour in the gas flow channel, respectively. The binary diffusion coefficient of oxygen and nitrogen $D_{O_2-N_2}$ is calculated using Chapman-Enskog equation (Perry and Green 1997)

$$D_{O_2-N_2} = 0.0018583 \left(\frac{1}{M_{O_2}} + \frac{1}{M_{N_2}} \right)^{0.5} \frac{T^{3/2}}{p |\sigma_{N_2-O_2}|^2 \Omega_{N_2-O_2}} \quad (7-19)$$

where M_{O_2} and M_{N_2} are the molecular weights of oxygen and nitrogen, respectively.

$\Omega_{N_2-O_2}$ is a dimensionless function of temperature and the intermolecular potential field of one molecule of O_2 and one of N_2 . $\sigma_{N_2-O_2}$ is the Lennard-Jones parameter.

And T is the temperature in K. The binary diffusion coefficient of oxygen and water

vapour is calculated from the critical pressure of these two gases ($p_{c,O_2} p_{c,H_2O}$) and temperature of them ($T_{c,O_2} T_{c,H_2O}$) using the Slattery-Bird equation (Bird *et al.* 1960)

$$D_{O_2-H_2O} = 0.000364 \left(\frac{T}{\sqrt{T_{c,O_2} T_{c,H_2O}}} \right)^{2.334} (p_{c,O_2} p_{c,H_2O})^{1/3} (T_{c,O_2} T_{c,H_2O}) \left(\frac{1}{M_{O_2}} + \frac{1}{M_{N_2}} \right)^{0.5} \quad (7-20)$$

Thus, the effective diffusion coefficient of oxygen relative to N_2 gas and water vapour with tortuosity of τ can be calculated from:

$$D_{O_2}^{eff} = \frac{\varepsilon_g D_{O_2}}{\tau} = \frac{\varepsilon(1-s)D_{O_2}}{\tau} \quad (7-21)$$

7.2.3 Governing equations in CCL

Substituting Eq. (7-9) and into Eq. (7-7) results in

$$\frac{d^2 F(s)}{dx^2} = -\frac{\mu_l M_{H_2O} (1-s) A_v^* i_{O_2}^0}{2\sigma F \varepsilon^{1.5} K^{0.5} s^4 \rho_l \cos \theta_c} \frac{C_{O_2}}{C_{O_2}^0} \left\{ \exp \left[\frac{(1-\alpha)nF}{RT} \eta \right] - \exp \left[-\frac{\alpha nF}{RT} \eta \right] \right\} \quad (7-22)$$

For a hydrophobic CCL ($\theta_c > 90^\circ$), the left term can be rewritten as:

$$\frac{d^2 F(s)}{dx^2} = \frac{d \left(\frac{dF(s)}{ds} \frac{ds}{dx} \right)}{dx} = (1.417 - 4.24s + 3.789s^2) \frac{d^2 s}{dx^2} - (4.24 - 7.578s) \left(\frac{ds}{dx} \right)^2 \quad (7-23)$$

For a hydrophilic CCL ($\theta_c < 90^\circ$), the left term can be rewritten as:

$$\frac{d^2 F(s)}{dx^2} = -[1.417 - 4.24(1-s) + 3.789(1-s)^2] \frac{d^2 s}{dx^2} - [4.24 - 7.578(1-s)] \left(\frac{ds}{dx} \right)^2 \quad (7-24)$$

Combining Eqs. (7-3), (7-4) and (7-6) together with the parameters determined in Section 7.2.2, it yields the governing equations for the CCL considering the cathode overpotential and oxygen concentration.

$$\frac{d^2\eta}{dx^2} = \rho_{\text{prot}}^{\text{eff}} (1-s) A_{\text{vO}_2}^* i_{\text{O}_2}^0 \frac{C_{\text{O}_2}}{C_{\text{O}_2}^0} \left\{ \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right] - \exp\left[-\frac{\alpha nF}{RT}\eta\right] \right\} \quad (7-25)$$

$$\frac{d^2C_{\text{O}_2}}{dx^2} = \frac{(1-s) A_{\text{vO}_2}^* i_{\text{O}_2}^0}{4FD_{\text{O}_2}^{\text{eff}}} \frac{C_{\text{O}_2}}{C_{\text{O}_2}^0} \left\{ \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right] - \exp\left[-\frac{\alpha nF}{RT}\eta\right] \right\} \quad (7-26)$$

With the value of the local overpotential along the CCL, the total cathode overpotential can be calculated as the potential difference between the GDL and the Nafion membrane. Due to the negligible resistivity of the electronic conductor within the CCL, the total cathode overpotential is given as

$$\eta_{\text{C}} = \eta|_{x=0} \quad (7-27)$$

7.2.4 Boundary conditions

In order to numerically solve the governing equations, the boundary conditions for the water saturation, cathode local overpotential and oxygen concentration at the CCL/GDL interface can be defined as:

$$\left\{ \begin{array}{ll} s = s_{\text{L}_{\text{CCL}}} & x = L_{\text{CCL}} \\ \eta = \eta_{\text{L}_{\text{CCL}}} & x = L_{\text{CCL}} \\ C_{\text{O}_2} = C_{\text{O}_2}^{\text{L}_{\text{CCL}}} & x = L_{\text{CCL}} \end{array} \right. \quad (7-28)$$

$$\left\{ \begin{array}{ll} \frac{ds}{dx} = \frac{ds}{dx}\bigg|_{\text{L}_{\text{CCL}}} & x = L_{\text{CCL}} \\ \frac{d\eta}{dx} = \frac{d\eta}{dx}\bigg|_{\text{L}_{\text{CCL}}} & x = L_{\text{CCL}} \\ \frac{dC_{\text{O}_2}}{dx} = \frac{dC_{\text{O}_2}}{dx}\bigg|_{\text{L}_{\text{CCL}}} & x = L_{\text{CCL}} \end{array} \right. \quad (7-29)$$

Pasaogullari and Wang (2004) studied the steady-state liquid water transport in gas diffusion layer of PEM fuel cells and developed an analytical approximation to

estimate the value of liquid saturation at the GDL/CCL interface ($s_{L_{CCL}}$), which is expressed as follows:

For the hydrophobic ($\theta_{GDL} > 90^\circ$) GDL,

$$s_{L_{CCL}}^4 (0.35425 - 0.8480s_{L_{CCL}} + 0.6135s_{L_{CCL}}^2) = \frac{-I}{2F} M_{H_2O} \frac{\mu_1 L_{GDL}}{\rho_1 \sigma (\varepsilon K)^{0.5} \cos \theta_{GDL}} \quad (7-30)$$

For the hydrophilic ($\theta_{GDL} < 90^\circ$) GDL,

$$s_{L_{CCL}}^4 (-0.241 + 0.668s_{L_{CCL}} - 0.6135s_{L_{CCL}}^2) = \frac{-I}{2F} M_{H_2O} \frac{\mu_1 L_{GDL}}{\rho_1 \sigma (\varepsilon K)^{0.5} \cos \theta_{GDL}} \quad (7-31)$$

Because no current is generated within the GDL, the oxygen is only consumed in the CCL. Firstly, oxygen transports from the gas flow channel to GDL surface via convection. Then the oxygen diffuses from GDL to CCL. During this transport process, molecular diffusion in the GDL can be expressed as:

$$J_{O_2}^{L_{CCL}} = \frac{I}{4F} = \frac{C_{O_2}^{ch} - C_{O_2}^{L_{CCL}}}{\frac{L_{GDL}}{D_{O_2} [\varepsilon(1-s)]^{1.5}} + \frac{1}{h_m}} \quad (7-32)$$

Thus, the oxygen molar concentration at the CCL/GDL interface can be calculated as

$$C_{O_2}^{L_{CCL}} = C_{O_2}^{ch} - \frac{I}{4F} \left[\frac{L_{GDL}}{D_{O_2} [\varepsilon(1-s)]^{1.5}} + \frac{1}{h_m} \right] \quad (7-33)$$

Because the current generated within the CCL is equal to the amount of oxygen diffused into the CCL at the CCL/GDL interface, the oxygen diffusion rate at the CCL/GDL interface can be expressed as:

$$\left. \frac{dC_{O_2}}{dx} \right|_{x=L_{CCL}} = -\frac{I}{4FD_{O_2}^{eff}} \quad (7-34)$$

Assuming that no electrochemical reactions happen within the GDL, the protonic current density is equal to zero and the electronic current is equal to the cell output

current at the CCL/GDL interface. Thus, first-order differential equation of local overpotential at the CCL/GDL interface is given as

$$\left. \frac{d\eta}{dx} \right|_{x=L_{\text{CCL}}} = 0 \quad (7-35)$$

The first-order differential equation for water saturation at the CCL/GDL interface was developed by Pasaogullari and Wang (2004) as

$$\left. \frac{ds_{\text{L}_{\text{CCL}}}}{dx} \right|_{\text{L}_{\text{CCL}}} = \frac{I}{2F} M_{\text{H}_2\text{O}} \frac{\mu_l}{\sigma(\varepsilon K)^{0.5} \cos \theta_{\text{GDL}}} \frac{1}{s_{\text{L}_{\text{CCL}}}^3 (1.417 - 4.240 s_{\text{L}_{\text{CCL}}} + 3.789 s_{\text{L}_{\text{CCL}}}^2)} \quad (7-36)$$

Table 7.1 Electrochemical and transport parameters

Parameters	Description of the parameters	Unit	Value	Reference
A_s	Catalyst surface area per unit mass of catalyst	m^2kg^{-1}	-	-
A_v	reactive surface area per unit volume	m^2/m^3	-	-
C_{O_2}	actual oxygen concentration	molm^{-3}	-	-
$C_{\text{O}_2}^0$	reference oxygen concentration	molm^{-3}	1.2	(Das <i>et al.</i> 2010)
$D_{\text{O}_2}^{\text{eff}}$	Effective diffusion coefficient of oxygen	-	-	-
D_{O_2}	Oxygen diffusion coefficient	-	-	-
$D_{\text{O}_2-\text{N}_2}$	Binary diffusion coefficient of oxygen and nitrogen	-	-	-
$D_{\text{O}_2-\text{H}_2\text{O}}$	Binary diffusion coefficient of oxygen and water vapor	-	-	-
F	Faraday's constant	Cmol^{-1}	96485	-
i_{prot}	Protonic current density	Acm^{-2}	-	-
i_{el}	Electronic current density	Acm^{-2}	-	-
$i_{\text{O}_2}^0$	Exchange current density	Acm^{-2}	-	-
K	Absolute permeability	m^2	7×10^{-13}	(Birgersson <i>et al.</i> 2005)

CHAPTER 7 MATHEMATIC ANALYSIS OF WATER TRANSPORT WITHIN
THE CCL OF PEM FUEL CELL

Table 7.2 Electrochemical and transport parameters

Parameters	Description of the parameters	Unit	Value	Reference
L_C	Thickness of catalyst layer	m	10^{-5}	-
m_{Pt}	Catalyst mass loading per unit area of cathode	kgm^{-2}	3.5	-
M_{H_2O}	Molecular weight of water	kg/mol	1.8×10^{-2}	-
M_{O_2}	Molecular weight of oxygen	kg/mol	3.2×10^{-2}	-
M_{N_2}	Molecular weight of nitrogen	kg/mol	2.8×10^{-2}	-
p_{c,H_2O}	Critical pressure of water vapour	atm	217.7	(Bird <i>et al.</i> 1960)
p_{c,O_2}	Critical pressure of oxygen	atm	49.7	(Bird <i>et al.</i> 1960)
p	Operating pressure	atm	1	-
p_g	Phase-averaged gas phase pressure	atm	1	-
p_{sat}	Saturation pressure of water at operating temperature	-	-	-
R	Universal gas constant	$Jmol^{-1}K^{-1}$	8.315	-
T	Temperature	K	296	-
T_{c,O_2}	Critical temperature of oxygen	K	154.4	(Bird <i>et al.</i> 1960)
T_{c,H_2O}	Critical temperature of water vapor	K	647.15	(Bird <i>et al.</i> 1960)

Table 7.3 Electrochemical and transport parameters

Parameters	Description of the parameters	Unit	Value	Reference
τ	Tortuosity	-	4	(Gostick <i>et al.</i> 2006)
$\Omega_{N_2-O_2}$	Dimensionless function of temperature and intermolecular potential field of one molecule of O ₂ and one of N ₂	-	0.8827	(Perry and Green 1997)
$\sigma_{N_2-O_2}$	Lennard-Jones parameter	-	3.6325	(Perry and Green 1997)
μ_l	Liquid water dynamic viscosity	PaS	0.355×10^{-3}	(Pasaogullari and Wang 2004)
ρ_l	Density of liquid water	Kgm ⁻³	983	(Pasaogullari and Wang 2004)
ε_l	Volume fraction of liquid water	-	-	-
ε	Porosity	-	0.5	(Pasaogullari and Wang 2004)
ρ_{prot}	Protonic resistivity	Ω m	0.059	(Das <i>et al.</i> 2010)
α	Apparent transfer coefficient	-	0.5	-
η_c	Cathode activation overpotential	-	-	-
σ	surface tension	N/m ²	0.0625	(Pasaogullari and Wang 2004)
θ_c	CCL surface contact angle	-	-	-
θ_{HI}	CCL hydrophilic surface contact angle	degree	70	(Park and Popov 2009)
θ_{HO}	CCL hydrophobic surface contact angle	degree	140	(Park and Popov 2009)

7.3 Results and discussion

The 1D governing equations expressed above can be numerically solved using all the physical and electrochemical parameters listed in Table 7-1. The liquid water saturation in the CCL is governed not only by the generation rate of the liquid water in the electrochemical reaction but also by the CCL and GDL hydrophobicity. As

described in Chapter 3, the CCL hydrophobicity can be modified with addition of different amounts of DSO in the CCL. In order to describe the effect of CCL hydrophobicity on the water saturation and water transport in the cathode more precisely, hydrophilic fraction, f_{HL} , as defined in Eq. (7-17) was adopted to simulate the different DSO loadings in CCL in the model.

7.3.1 Water saturation and oxygen concentration at the GDL/CCL and CCL/membrane interface

For simplicity, it is assumed that no liquid water saturation is present in the gas flow channel. During the fuel cell operation, the liquid water transports from the reaction sites in the CCL to the gas flow channel through the GDL layer. Because no electrochemical reactions happen within the GDL, the total mass flux of the liquid water in GDL is equal to the sum of water produced at the CCL. Thus, the water saturation and oxygen concentration at the GDL/CCL interface can be easily calculated according to the Eqs. 7-30, 7-31 and 7-33. Fig. 7.3 and 7.4 illustrate the water saturation and oxygen concentration at the GDL/CCL interface as a function of current density with different GDL contact angles, respectively. It is found that the liquid water saturation increases rapidly at the GDL/CCL interface for the GDL with contact angle of 91° . The occupation of liquid water within the pores will significantly limit the oxygen transport in the cathode. Thus, it is not surprised to see in Fig. 7.4 that the concentration of oxygen at the GDL/CCL interface with GDL contact angle of 91° drops rapidly to zero, leading to a low limiting current density of less than 400 mA/cm^2 . In general, the higher the GDL contact angle, the lower the

water saturation and higher the oxygen concentration at the GDL/CCL interface will be, and vice verse.

Fig. 7.3 Water saturation at the GDL/CCL interface of a PEM fuel cell as a function of current density in the condition with different GDL contact angles

Fig. 7.4 Oxygen concentrations at the GDL/CCL interface as a function of the current density in the condition with different GDL contact angles

7.3.2 Distribution of local overpotential, local current density and water saturation along the CCL thickness

The distribution of local overpotential, local current density and water saturation can be obtained from the 1D model with the governing equations considering the electrochemical reactions, oxygen transport and water transport in the CCL. At a constant temperature, the water properties, such as water surface tension and viscosity, remain unchanged. Thus, the transport of the liquid water and the local overpotential in CCL relies strongly on the CCL characteristics. As shown in Fig. 7.5, with the same output current density, the higher the hydrophilic fraction in the CCL, the higher the local overpotential will be along the CCL. This is because that the higher hydrophilic fraction leads to higher water saturation in the CCL, which occupies the pores in CCL and significantly blocks the active surface sites, thus resulting in higher local overpotential. It is worthwhile to notice that there is a significant decrease of local overpotential from hydrophilic fraction of 0.8 to 0.6. However, the local overpotential for cathode with hydrophilic fraction of 0.4 is only slightly decreased with the increasing of hydrophilic fraction to 0.2.

The profile of the dimensionless local current density along the CCL is plotted in Fig. 7.6 as a function of output current density. It is found that the smaller the current density, the more homogeneously distributed is the reaction rate and, thus the catalyst utilization in the CCL. With the increase of the current density, more and more current is generated close to the CCL/membrane interface. At low current densities, small amount of oxygen is consumed and ohmic loss along the CCL is negligible. Thus, the whole CCL is utilized for the electrochemical reaction. However, at high current densities, the ohmic loss due to the proton transport from the electrolyte to the

reaction sites within the CCL becomes significant, limiting the electrochemical reactions to the CCL/membrane interface. In order to further understand the factors that affect the distribution of local current density, the dimensionless local current density along the CCL as a function of protonic resistivity was simulated and shown in Fig. 7.7. With high protonic resistivity, only a small layer of CCL close to the membrane contributes actively to the electrochemical reactions due to the difficulty for the proton transporting from the membrane to the active sites for reaction. However, low protonic resistivity significantly reduces the barrier for the proton transport, thus extending the electrochemical reactions to the whole CCL.

Fig. 7.5 Distribution of local overpotential along the CCL thickness

Fig. 7.6 Normalized current density profile across the catalyst layer thickness with hydrophilic fraction in CCL of 0.4

Fig. 7.7 Normalized current density profile across the catalyst layer thickness as a function of protonic resistivity

Fig. 7.8 Effect of hydrophilic fraction on the water saturation along the CCL thickness at room temperature

It is well known that the hydrophobic materials help to drain water out of the cathode in the PEM fuel cell. Fig. 7.8 shows the effect of hydrophilic fraction in CCL on the distribution of water saturation along the CCL. Three phenomena can be found from the results that (i) the CCL/membrane interface has highest water saturation in the CCL for all CCLs with different hydrophilic fractions; (ii) the higher the hydrophilic fraction, the higher water saturation along the CCL will be at the same current density; and (iii) there exists a minimum water saturation value along the CCL, which shifts to the membrane side with the increase of the hydrophilic fraction. As shown in Fig. 7.6, the current density is equal to zero at the CCL/membrane interface, which means that

no water is electrochemically produced at the interface. Thus, the high water saturation at the CCL/membrane interface could be due to the expelling of the electrochemically water product both to the membrane side and GDL side by the CCL. If no back diffusion is considered, the liquid water will accumulate at the CCL/membrane interface, leading to the high water saturation at the interface. This speculation is further supported by the observed minimum water saturation value along the CCL. The shift of location for the minimum water saturation along the CCL to the membrane side indicates that the expelling of liquid water out of CCL to the gas diffusion channel through the GDL becomes difficult with the increase of hydrophilic fraction in the CCL. In another word, it is easy to be flooded for the CCL with high hydrophilic fraction.

The effects of current density and operating temperature on the liquid water saturation along the CCL are shown in Fig. 7.9 and 7.10. When the fuel cell operates at room temperature with CCL hydrophilic fraction of 0.4, the water saturation along the CCL increases with the increase of current density. This is understandable that if the water can not properly expelled out of CCL, liquid water will accumulate in the CCL and flooding happens at high current density where more water has been generated. Under a typical CCL hydrophilic fraction and current density, lower water saturation along the CCL is found at higher operating temperature, indicating that high operating temperature can alleviate the flooding phenomenon in the cathode (Fig. 7.10). In this modeling analysis, the fuel cell is assumed to operate under steady state condition and the membrane is fully humidified so that the active surface area and ionic/electronic resistivity are uniform throughout the CCL. However, in the practical applications, one should bear in mind that the dry out effect of the membrane at high operating

temperature or/and low current density should also be considered, where the electrochemically water product is not sufficient to maintain the hydration of the membrane.

Fig. 7.9 Effect of current density on the water saturation along the CCL thickness at room temperature with CCL hydrophilic fraction of 0.4

Fig. 7.10 Effect of temperature on the water saturation along the CCL thickness

7.3.3 Cathode overpotential

The cathode overpotential vs. current density is plotted in Fig. 7.11 as a function of different CCL hydrophilic fractions for an oxygen partial pressure of 0.21 atm in the gas flow channel. In general, the higher the CCL hydrophilic fraction, the higher the cathode overpotential will be. With the increase of the CCL hydrophilic fraction, the increase of cathode overpotential is rather slow at low current densities but has become significant fast at high current densities. This is because at low current densities, the cathode overpotential is dominated by the activation polarization and no water flooding happens. Hence, when the current density is lower than 200 mA/cm^2 , the change of the cathode overpotential is not sensitive to the CCL wettability. However, at high current densities, more oxygen is required for the electrochemical reactions while more water is produced during the reaction. Thus, the cathode overpotential is controlled by the transport of oxygen from the gas diffusion channel to the reactions in the CCL. As shown in above, the CCL with high hydrophilic fraction has high water saturation along the CCL, thus poor ability to drain water out of CCL. As a result, the limiting current densities significantly reduce with the increase of the CCL hydrophilic fraction. The flooding phenomenon happens in cathode could be attributed to two factors: (i) significant reduction of active surface area due to the coverage of liquid water and (ii) slow oxygen transport due to the occupation of liquid water in the pores. The former factor mainly affects the activation polarization region, while the latter dominates the cathode overpotential at high current densities.

Fig. 7.11 Relations between cathode overpotential and current density for the different hydrophilic fractions

Chapter 8. Conclusions and recommendations

In this thesis, a novel anti-flooding cathode, which improves the overall fuel cell performance, has been developed and characterized using mercury porosimetry, SEM, EDX, contact angle, steady state polarization, transient current-step and electrochemical impedance spectroscopy. The effect of the hydrophobic dimethyl silicone oil (DSO) in the cathode catalyst layer (CCL) on the performance of the PEM fuel cells has been systematically investigated. The performance of the PEM fuel cells with different CCLs in various cathode structures under different water conditions has been explored and compared. Subsequently, a mathematic model has been developed to fundamentally understand the role of CCL properties on the water management and fuel cell performance.

8.1 Conclusions

The objectives of this work are to develop anti-flooding cathodes by optimizing the properties of the cathode catalyst layer (CCL); to investigate the mechanisms of water transport within the cathode; and to establish a mathematic model to analyze the water transport within the CCL of the PEM fuel cell. They have been met in this study. Based on the experimental results and the modeling analysis of the CCL, following conclusions can be drawn:

- (1) The cathodes with DSO loadings of 0, 0.25, 0.4, 0.5 to 0.65 mg/cm² in the CCL were fabricated by incorporating DSO into the cathode catalyst layer during the ink preparation step. All the electrodes were characterized using contact angle,

mercury porosimetry, SEM and EDX. The contact angle measurement indicated that the hydrophobicity of the CCL increased with the increase of the DSO loadings. The SEM images showed that the DSO can dramatically change the CCL morphology. With the DSO loading of 0.5 mg/cm^2 in the CCL, a number of pores with diameter around $0.1\text{-}3 \text{ }\mu\text{m}$ were observed to be homogeneously distributed in the CCL. The porosimetry study showed that the DSO not only occupied the big pores between the catalyst agglomerates but also penetrated into the small pores among the carbon particles in the agglomerates, which is benefit to prevent water condensation whereas still maintaining high oxygen transport rate to the reaction sites.

- (2) The effects of DSO loadings in the CCL on the performance of the PEM fuel cells were investigated systematically. The single fuel cell was tested in both H_2/air and H_2/O_2 systems at room temperature. The results showed that the addition of DSO into the CCL can prevent the cathode from flooding effectively at high current density and facilitate the oxygen transport, thus significantly improving the performance of a PEM fuel cell. An optimal DSO loading in the CCL was found to be 0.5 mg/cm^2 in both systems. The highest maximum power density of 356 mW/cm^2 in H_2/air (or 709 mW/cm^2 in H_2/O_2) was achieved at room temperature with this DSO loading, significantly improving from 144 mW/cm^2 in H_2/air (or 400 mW/cm^2 in H_2/O_2) of the fuel cells with a normal cathode, respectively. However, excessive DSO loading, i.e., 0.65 mg/cm^2 in this study, might block the pores of the CCL, leading to a lower limiting current density and maximum power density.

Furthermore, the stable performance for MEAs with 0.5 mg/cm^2 DSO loaded cathode for 40 hours implied that the DSO could be constrained in the CCL for long time. However, transient current analysis suggested that the high hydrophobicity in the CCL can delay the hydration of the electrolyte, especially at low current density with low humidification. The EIS measurements at different voltages also showed that the DSO loaded CCLs were sensitive to the water content at low humidifying conditions and low current density. The charge transfer resistances at different voltages for the MEA with 0.5 mg/cm^2 DSO loaded cathode can be satisfactorily explained in terms of the CCL thin film/flooded agglomerate model. The optimized MEA with 0.5 mg/cm^2 DSO loaded cathode was applied to develop a planar self-breathing two cell stack. The improved water management of the DSO-loaded cathode is believed to be the main factor for the excellent performance of the self-breathing PEM stack.

- (3) The effects of temperature on the polarization behavior of the fuel cells with DSO loaded cathode have been investigated. The results of the fuel cells with 0.5 mg/cm^2 DSO loaded cathode and normal cathode were compared at three cell temperatures of 35°C , 50°C and 60°C . The results indicated that DSO loaded cathode can also improve the performance of a PEMFC at elevated temperatures. Especially, when the fuel cells operated in the humidified air, i.e. the cathodes were fed with over-saturated air, the performances of the fuel cell with normal cathode were much worse in the humidified air compared with the dry air in the high current density region for all three operating temperatures. Under this over-saturated condition, the DSO loaded cathode showed more advantageous in repelling water out of the CCL than the normal cathode. The performances of the

fuel cell with DSO loaded cathode were even slightly higher at 35°C in humidified air than those of in the dry air.

- (4) The role of micro-porous layer (MPL) is found to be critical for the efficient water management in the PEM fuel cell. The porosimetry study showed that the MPL can create a number of pores with size range in 0.02 μm to 0.5 μm which is beneficial for the water removal from cathode. Since the pore size in the CCL is in the same magnitude with the pores in the MPL, the hydrophobic CCL modulated by DSO can function as a watershed as the MPL. The electrochemical behaviors of the fuel cells with normal CCL without MPL, normal CCL with MPL and DSO loaded CCL without MPL have been compared under the same operation conditions. The limiting current density of the fuel cell with normal CCL with MPL reached 900 mA/cm^2 which is more than two times higher than that of the fuel cell with normal CCL without MPL of 400 mA/cm^2 . The fuel cell with DSO loaded CCL without MPL has slightly poorer performance at low current density, but it prevails the fuel cell with normal CCL with MPL at high current density.

The EIS measurements showed that the charge transfer resistance for the DSO loaded cathode decreased rapidly with the increasing of the water level in the CCL. The mass transport resistances of the fuel cell with normal CCL on MPL were found to be higher than those of the fuel cell with DSO loaded CCL without MPL, which could be due to the additional diffusion resistance of oxygen through MPL. The polarization curves of the fuel cells with three types of cathodes in dry H_2 /dry air demonstrated that ohmic resistances for the fuel cell with normal CCL with MPL and DSO loaded cathode without MPL decreased with the increasing of

overpotential. These phenomena could be explained by the back flow of the generated water to the electrolyte so as to decrease the electrolyte resistance.

(5) The effect of the CCL hydrophobicity on the performance of the PEM fuel cell with MPL in the cathode GDL has been explored under various operating conditions. With the combined effect of the MPL and the hydrophobic CCL, the fuel cell with DSO-loaded CCL on the top of MPL has higher limiting current density due to its higher ability to prevent cathode flooding when the gas was sufficient humidified. However, when this MEA with DSO loaded CCL on MPL operated in dry gases, high ohmic resistance predominate the cell performance at low current density zone due to the poor water retention ability of the cathode. Hence, one should bear in mind that the hydrophobic level of the CCL is critical and must be carefully controlled to balance the conflicting requirements of the electrolyte hydration and the cathode anti-flooding. The polarization analysis indicated that the hydrophobic CCL and MPL significantly reduced oxygen transport limitation in the CCL by controlling liquid water saturation in the cathode.

(6) A mathematical model describing the major transport phenomena in cathode catalyst layer (CCL) of a PEMFC has been developed. It reveals how the hydrophobicity of the CCL surface steers water, oxygen concentration and current density distributions in the CCL, thus affecting the performance of a PEMFC. The role of wetting properties of the CCL on controlling the water transport for some operation conditions has been simulated. The parametric studies show that a CCL with high hydrophobicity can significantly reduce water saturation along the CCL,

thus increasing the limiting current density. According to this model, highest water saturation is found at the CCL/membrane interface along the CCL in all of the simulated cases. The hydrophobicity of CCL will determine the amount of water that push to the GDL. In summary, this one-dimensional CCL model can help to fundamentally understand the water transport within the CCL and optimize the operating conditions and CCL properties for improved fuel cell performance.

8.2 Recommendations

The following subjects are suggested for further development:

- (1) The addition of DSO into the cathode catalyst layer can significantly improve the water management and the oxygen transport inside the cathode of a fuel cell. The mechanism of increasing oxygen transport should be explored by more fundamental means. The approach using a rotating Pt disk electrode with a thin film of DSO loaded catalyst layer to evaluate the diffusion coefficient of oxygen is suggested.
- (2) Modeling is a useful designing tool to guide the experiment and understand the mechanism of a fuel cell. The present one-dimensional two-phase mathematical model described the major transport phenomena in cathode catalyst layer (CCL) of a PEMFC. To increase the accuracy of the prediction by the modeling work, two-dimensional or even three-dimensional two-phase mathematical model is recommended to investigation the effect of the addition of DSO into the CCL.

List of publications

- (1) Li, A. D., M. Han, S. H. Chan, N. T. Nguyen, (2010). "Effects of hydrophobicity of the cathode catalyst layer on the performance of a PEM fuel cell." Electrochimica Acta **55**(8): 2706-2711.
- (2) Li, A. D., S. H. Chan, N.-T. Nguyen, (2009). "Anti-flooding cathode catalyst layer for high performance PEM fuel cell." Electrochemistry Communications **11**(4): 897-900.
- (3) Li, A. D., S. H. Chan, N.-T. Nguyen, (2007). "A laser-micromachined polymeric membraneless fuel cell." Journal of Micromechanics and Microengineering **17**(6): 1107-1113.
- (4) Li, A. D., M. Han, S. H. Chan, N. T. Nguyen, "Effects of cathode structure on water management of PEM fuel cell." in preparation.
- (5) Li, A. D., M. Han, S. H. Chan, N. T. Nguyen, "Effects of DSO on the cathode catalyst layer on the transient performance of PEM fuel cell." in preparation.

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