Investigation of performance and microstructure of membrane-electrode-assembly in PEMFC

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**NANYANG
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**INVESTIGATION OF PERFORMANCE AND
MICROSTRUCTURE OF MEMBRANE-
ELECTRODE-ASSEMBLY IN PEMFC**

HAN MING

SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING

2007

Investigation of Performance and Microstructure of Membrane-Electrode-Assembly in PEMFC

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School of Mechanical & Aerospace Engineering

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ABSTRACT

Abstract

In this study, a carbon-filled gas diffusion layer (CFGDL), and a novel self-humidifying membrane electrode assembly (MEA) for proton exchange membrane fuel cell (PEMFC) were developed for improvement of the performance of PEMFC. The studies are included in detail as follows:

1. A new structural design of gas diffusion layer (GDL) - CFGDL is made of electrical conductive macro-porous carbon paper filled with a mixture of conductive carbon powder and hydrophobic polymer (PTFE). The systematic study on the properties of CFGDLs and their electrodes with various physical analysis techniques and electrochemical characterizations were carried out in comparison with conventional one-layer GDL, dual-layer GDL, and gained an insight into the relationship between the electrode performance and GDL structure.
2. The effects of material composition in CFGDL on the microstructure and performance of CFGDL were studied. The experimental results showed that the carbon loading in the CFGDL plays a critical role in the electrode performance and Pt utilization, but the PTFE content in the CFGDL has lesser influence.
3. The effect of PTFE content on the mass transport in the CFGDL was studied. It was found that the PTFE content in CFGDL significantly affected the contact angle (hydrophobic property) and water uptake (immobile liquid saturation) of CFGDL. The analysis by a theoretical model developed for cathode flooding, in which the water saturation is incorporated, shows that the mass transport limitation of fuel cells at high current density is attributed to the water flooding when using CFGDL with a lower PTFE content.

ABSTRACT

4. Based on a new self-humidifying mechanism proposed for PEMFC, a self-humidifying MEA was developed. The MEA consists of an anode with doped nano-scale hygroscopic oxide (silica), a cathode either with or without doped nano-scale hygroscopic oxide and a Nafion membrane located between them. Not only does the nano silica particles covered with a Nafion polymer layer serve the function of the proton transport but also play a role of water absorption for hydrating the Nafion polymer layer. A hydrophobic electrode protonized by Nafion – silica suspension as the anode in the fuel cell has achieved a significant self-humidifying effect.

5. A new macro-model for predicting the possibility of the self-humidifying operation in PEMFC was developed based on the work reported by Chan et al. [2006] and Yu [2000]. The suitable range of operating temperatures and air stoichiometric number under different condition could be estimated using this model.

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LIST OF SYMBOLS

List of Symbols

a	Active surface area (M^2g^{-1})
b	(a) Tafel constant (mVdec^{-1}) (b) ratio of actual area of contact between the liquid drop and the solid portion of surface to the projected area
B	Constant related to mass transport phenomena
C_{O_2}	Oxygen concentration (mol cm^{-3})
$D_{i,j}$	Binary diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
d	(a) Diameter of platinum particles ($\text{\AA}$), and (b) Pore diameter (μm)
d_f	Density of the conducting filler (g cm^{-3})
d_{pore}	Diameter of pore (μm)
$d_{i,a}$	Average diameter of local pores (μm)
$d_{t,a}$	Average diameter of total pores (μm)
E	Cell potential (V)
E_{rev}	Reversible potential of the cell (V)
F	Faraday constant, 96487 (C mol^{-1})
$F_{wetting}$	Wetting force (repelling or attracting force) (dynes cm^{-2})
$F_{buoyancy}$	Buoyancy force (dynes cm^{-2})
f	Ratio of the water removal from the anode to total water generated and carried by the inlet air at the cathode
f_1	Fraction of the GDL surface occupied by solid
f_2	Fraction of the GDL surface occupied by void
G	Gibbs free energy (J mol^{-1})
H_{O_2}	Henry's constant ($\text{atm cm}^3\text{mol}^{-1}$)
i	Current density (mAcm^{-2} , Acm^{-2})
i_0	Exchange current density (mAcm^{-2} , Acm^{-2})
i_L	Limiting current density (mAcm^{-2} , Acm^{-2})
k	Permeability of GDL (m^2)
k_k	Kozeny constant, (= 5)

LIST OF SYMBOLS

L	Thickness of sample (mm)
$L_{l,s}$	Length of the liquid-solid interface (cm)
l	Thickness of sample (cm)
M	Molecular weight (g)
m_c	Loading of carbon powder (mg cm^{-2})
m_f	Loading of conducting filler (mg cm^{-2})
m_p	Loading of polymer binder (mg cm^{-2})
n	Electrons per molecule oxidized or reduced
Q_H	Columbic charges for H_2 adsorptions (mC cm^{-2})
P	(a) applied pressure (dynes cm^{-2}) (b) reactant gas pressure (atm)
p_{H_2}	H_2 partial pressure (atm)
p_{O_2}	O_2 partial pressure (atm)
R	(a) resistance ($\Omega \text{ cm}^2$) (b) ideal gas constant, $8.314 \text{ (J mol}^{-1}\text{K}^{-1})$
$R_{\text{ASR},T}$	Area specific resistance in through-plane ($\Omega \text{ cm}^2$)
RH	Relative humidity
Sto	Stoichiometric number
s_l	Water/liquid saturation
s_{im}	Immobile saturation
s_m	Mobile saturation
T	Temperature ($^{\circ}\text{C}$, K)
V_f	Volume fraction of the conducting filler
V_m	Volume fraction of the macro-porous substrate
V_{GDL}	The geometric volume of GDL (cm^3)
W	Weight of samples (g)
w_{Pt}	Pt loading on electrode (mg cm^{-2})
x	(a) weight fraction of hydrophobic polymer (b) mole fraction of species

LIST OF SYMBOLS

Greek

α	Transfer coefficient
β	Volume ratio of N ₂ to O ₂ in the air (= 3.762)
δ_d	Thickness of diffusion layer (cm)
ε	Porosity of porous matrix
ε_0	Porosity of carbon paper before hydrophobic treatment
ε_g	Gas volume fraction
ε_l	Liquid volume fraction
ε_i	Local porosity
ε_t	Total porosity
Φ_w	Water uptake of Nafion-silica composite film (g)
η	Overpotential (V)
κ	Conductivity of membrane (S cm ⁻¹)
λ	Water content of membrane
θ	Contact angle
ρ_{Pt}	Pt density (21.4 g cm ⁻³)
ρ_w	Density of water (1 g cm ⁻³)
ρ_f	Resistivity of conducting filler (Ω cm)
ρ_m	Resistivity of macro-porous substrate (Ω cm)
ρ_T	Resistivity in through-plane (Ω cm)
σ	Surface tension, 480 dynes cm ⁻¹ for mercury, 72 dynes cm ⁻¹ for water
τ	Tortuosity factor
ξ	Loading ratio of conducting particle to polymer binder

Subscripts

A	Air
a	Anode side
act	Activation
c	(a) contact, and (b) cathode

LIST OF SYMBOLS

con	Concentration
c,m	Measured contact
cell	Fuel cell
CP	Carbon paper
diff	diffusion
e	(a) electrode, and (b) electrochemically
g	Gaseous
H	Hydrogen
HP	Hydrophobic polymer
in	Inlet
m	Membrane
ohm	Ohmic
out	Outlet
w	Water

Superscripts

ch	Channel
crit	Critical
f	Flow field
in	Inlet
out	Outlet
ref	Reference
sat	Saturation

CHAPTER 1 Introduction

CHAPTER 1 Introduction

1.1 Background

Fuel cells are electrochemical devices that directly convert chemical energy in fuels into electrical energy without combustion process. Compared with internal combustion engines, fuel cells have significant advantages, such as high-energy conversion efficiency without the limitation of Carnot cycle, high power density, very low greenhouse gas emission, quiet operation, etc. Therefore, it is considered to be a new type of power generation technologies in the 21st century, and will have promising applications in stationary and mobile power sources, electric vehicles, submarines, spaceflight etc.

According to the electrolyte materials used in a fuel cell, fuel cells can be classified into five most common types: 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). Of these types, PEMFC, PAFC and AFC operate at temperature between 60 ~200 °C whereas the operating temperature of MCFC and SOFC is 600 ~ 1000 °C [EG & G services, 2000].

The proton exchange membrane fuel cell (PEMFC), also called the “solid polymer fuel cell” (SPFC), was first developed by General Electric in the USA in the 1960’s for use by NASA on their first manned space vehicle. It was also used to provide the astronauts with clean drinking water. The membrane used was a polystyrene sulfonate (PSS) polymer, which proved not stable enough. This was one of the major reasons for NASA to opt for the AFC system for its later missions [Maget, 1968; Warshay & Prokopius, 1989; Zawodzinski et al., 1993].

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A major breakthrough in the field of PEMFCs was when the General Electric Company substituted the polystyrene sulphonic acid membrane with DuPont Chemical's Nafion® membranes in PEM fuel cell [Eisenber & King, 1997; Yeo & Eisenberg, 1977]. The lifetime of PEM fuel cells with this kind of perfluorinated sulphonic acid membranes was greatly enhanced to 60,000 hrs [Mehta & Cooper, 2002; Kerres, 2001].

In the mid 1980's, an ingenious method was developed by Raistrick et al. [1989] (Los Alamos National Laboratory), which made it possible to make a 10 – fold reduction of the platinum loading in the electrode and still retain the performance of oxygen electrode as with the high platinum loading. Therefore, PEMFC technology experienced a renaissance in the form of introduction of low platinum loading electrodes, and further in the early 1990's with the invention of thin film electrodes [Gottesfeld & Wilson, 1992 (1); Fedkiw & Her, 1989].

At the moment, fuel cell technology is maturing towards commercialization, but work still has to be done in many fields. Because a fuel cell is supplied with fuel and oxygen (air) from an external source, the reactants have to be supplied adequately to the electrode, and the reaction products have to be removed from the cell immediately. For PEM fuel cell, the mass transfer phenomena in the fuel cell should be investigated. Water management in particular on the oxidant side (cathode) has a major impact on cell performance and lifetime. In a typical PEM fuel cell, there must be sufficient water content in the polymer electrolyte; otherwise the conductivity will decrease. However, too much water would lead to a significant loss in performance due to the flooding of pores in the gas diffusion layer by the liquid water inhibiting access of the oxidant gas to the catalyst. A balance in the water content is therefore

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needed, which takes care to achieve. Hence, fundamental researches into the electrolyte membrane physicochemical properties with the fuel cell, optimization of structure, composition and operational conditions of the gas diffusion electrodes and membrane/electrode assembly (MEA) construction for attaining high power density and high energy conversion efficiency are needed in order to fundamentally understand the processes involved in the mass transports.

1.2 Basic operating principle of PEM fuel cell

1.2.1 PEM fuel cell structure and electrochemical reactions

Fig.1-1 shows the main functional parts of one unit of PEM fuel cell, which consist of flow-field plates (forming both anode and cathode chambers, also used as current collectors), anode, cathode and polymer electrolyte membrane. The combination of the membrane and the two Pt/C porous electrodes (anode and cathode) of this unit cell is usually referred to as the membrane electrode assembly (MEA), which is the most important part of the fuel cell system. The Pt/C porous electrode, referred to as the gas diffusion electrode, is formed by a catalyst layer and backing layer (also called gas diffusion layer, *i.e.* GDL).

As the reactant gases flow through the flow field channels of the fuel cell, gas molecules diffuse through the gas diffusion layer to the catalyst layer. At the anode, hydrogen is oxidized to release two electrons and two protons:

The protons are conducted through the proton exchange membrane from the anode to the cathode and the electrons travel through the external circuit, in which the electric current is formed, from the anode to the cathode. At the cathode, oxygen is reduced:

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The overall cell reaction is:

Fig. 1- 1 A schematic representation of a PEM fuel cell showing the reactant/product and proton conduction flow paths

The overall reaction in Eq. (1-3) can be used to produce both electrical energy and heat. The theoretical maximum work available from a fuel source is related to the isothermal free energy of the reaction with the voltage of a fuel cell, i.e.

$$\Delta G = -nFE \quad (1-4)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, and E is the voltage of the cell for thermodynamic equilibrium in the absence of a current flow.

1.2.2 Fuel cell performance

The ideal standard potential of a hydrogen/oxygen fuel cell, which is obtained for standard state conditions, (25 °C and 1 atm) is 1.23 V with liquid water product.

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However, the actual cell potential is decreased from its equilibrium potential because of irreversible losses as shown in Fig.1-2.

Fig. 1- 2 Typical polarization curve of a PEM fuel cell and predominant loss mechanisms in various current density regions (ideal and actual fuel cell voltage/current characteristics)

Several sources, which contribute to irreversible losses (referred to as polarization) in practical fuel cell, can be summarized as follows:

1. **Activation polarization:** activation polarization is caused by the sluggish kinetics of the reactions taking place on the active surface of electrodes. At low current densities, the shape of the curve is primarily determined by the cathode activation polarization. The cathode is generally the performance-limiting electrode of the PEM fuel cell, because the exchange current density of oxygen reduction reaction is low as compared to that of hydrogen oxidation. The exchange current density of the cathode reaction is approximately several orders of magnitude lower than that of the anode reaction [Appleby & Foulkes, 1989].

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2. Ohmic polarization: it is referred as to the resistance losses, which change directly with the current over the whole range since cell resistance remains essentially constant. The intermediate region of the curve in Figure 1.2 is linear and largely affected by resistance losses that consist of the resistance of membrane and the bulk resistances and contact resistances of the construction materials. The largest part of resistance losses is from the membrane when hydrated improperly. Minimization of resistance loss in the membrane requires effective water management.
3. Concentration polarization: it is referred as to the reactant transport losses, which occur over the entire range of current density, but become prevailing at high current density where the insufficient reactant flows are provided to the cell reaction sites. At practical current densities, slow transport of reactants and product to/from the electrochemical reaction sites is a major contributor to the irreversible losses. This usually happens when the cathode is severely flooded.
4. Internal current loss: also note that at open circuit, the cell voltage is much lower than the theoretical voltage, often attributed to a mixed potential caused by hydrogen crossover through the membrane [Larminie and Dicks, 2000] and very small amounts of electron conduction in the membrane without any useful work produced. This internal current arises the cell potential drop like the current is drawn from a fuel cell, even if the cell is in open circuit. This loss affects the performance of a fuel cell most at open circuit but is insignificant at higher current density because the crossover current density is very small, usually less than 10 mAcm^{-2} [Larminie and Dicks, 2000].

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1.3 The challenges in the development of PEM fuel cell

In hydrogen / air PEM fuel cell, the activation and concentration polarizations at cathode are much more significant than those at the anode [Paulus et al, 2001; Gottesfeld & Zawodzinski, 1997; Parthasarathy et al, 1992]. It is because the kinetics of hydrogen oxidation reaction (HOR) is much faster than the kinetics of oxygen reduction reaction (ORR) as mentioned above; and the hydrogen diffusivity is several times that of oxygen so that hydrogen concentration polarization is neglected.

At the heart of the PEMFC is the membrane electrode assembly (MEA) which consists of a proton exchange membrane, anode and cathode as shown in Fig.1-1. A more detailed schematic of an electrode (the cathode) is illustrated in Fig.1-3. The electrode provides the framework for the following transport processes:

1. The transport of the reactants and products to and from the catalyst layer, respectively.
2. The conduction of protons between the membrane and catalyst layer.
3. The conduction of electrons between the current collectors and the catalyst layer via the gas diffusion layer.

An effective electrode is one that correctly balances each of the transport processes. One challenge for transport processes is the efficient delivery of oxygen to the catalyst layer and adequate removal of water from the electrode. This is the two-phase flow and transport problem in porous gas diffusion electrodes. For instance, the fast removal of water from the electrode would decrease the fuel cell performance due to electrolyte dry out; the slow removal water could cause the liquid water to be accumulated in the electrode to hinder the delivery of oxygen to the catalyst layer. To

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efficiently conduct protons, the membrane and catalyst layers must maintain high levels of humidification, which is another challenge for a PEMFC. The introduction of water into the fuel cell from the external humidification would increase the complication of the system, thus reducing the overall efficiency of the PEM fuel cell.

To establish the optimal electrochemical kinetics, which is achieved when a three-phase interface exists between the membrane, the electrode and the reactant gas, is also a challenge. Only catalyst located in the three-phase interface region is electrochemically active and not all catalyst present is utilized.

Fig. 1- 3Transport of gases, proton, and electrons in a PEMFC cathode

1.4 Objectives of research project

The objective of this study is (1) to develop a new generation carbon-filled gas diffusion layer (CFGDL) and a new self-humidifying electrode for PEM fuel cell; (2) to systematically, in detail, study the physicochemical properties of the CFGDL and its MEA through various characterization methods in comparison with the conventional one-layer and dual-layer GDL; (3) to propose a new humidification mechanism and investigate physicochemical properties of the self-humidifying electrode for an H_2 / air PEM fuel cell.

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1.5 The scope of the research project

1. A new generation CFGDL will be developed using the lower density and more porous carbon paper filled with the mixture of carbon powder and hydrophobic binder, based on the GDL invented by Campbell et al. To understand fundamentally, in detail, the physical properties and electrochemical behaviors of the CFGDL, various microstructural characterizations (SEM, EDX, FESEM, TEM, MIP) and electrochemical characterizations (CV, EIS, steady-state polarization) will be done in comparison with the one-layer and dual-layer GDLs. The relationship between the surface morphology and microstructure of the CFGDL and the electro-catalytic activity of the cell and the analysis of kinetic parameters of the electrode with CFGDL will be investigated. Empirical parameters for the fuel cell modeling research and information for the ideal GDL design for PEMFC will be obtained from the experiment.

2. Fabrication of carbon-filled gas diffusion layer (CFGDL) and investigation of the effect of carbon loading and PTFE content in CFGDL on the cell performance will be carried out in order to optimize the composition of carbon/PTFE through the evaluation of properties such as electrical resistance, structural morphology & micro-structure, catalyst utilization and fuel cell performance, and to understand the relationship between the morphology and microstructure of the CFGDL and the fuel cell performance.

2. Effect of PTFE content on the mass transport in the gas diffusion layer for polymer electrolyte fuel cells will be quantitatively studied. The important physical and structural parameters such as water saturation, liquid volume fraction & gas volume fraction, contact angle of the GDL for the investigation of two-phase flow and

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transport in the GDL will be obtained from the experimental investigation, using the mercury intrusion porosimetry (MIP), water uptake measurement and the contact angle measurement. The relationship between the cell performance and the physical and structure parameters of the GDLs will be investigated.

3. Self-humidification for fuel cells will be studied to improve the water management in the membrane electrode assembly (MEA) for polymer electrolyte fuel cell, especially under ambient pressure conditions. A Nafion- hygroscopic oxide (*i.e.* silica) solution containing highly dispersed nano-sized SiO_2 particles will be used in the electrode for this kind of self-humidification. The effects of the silica content in the self-humidifying anode and the thickness of Nafion membrane on the fuel cell performance will be also investigated to optimize the self-humidifying electrode for a fuel cell.

4. A new macro-model for predicting the possibility of the self-humidifying operation in PEMFC will be developed to theoretically understand the mechanism of the fuel cell “out of action”. The suitable operating temperatures and air stoichiometric number under different condition will be estimated based on the model. The important relationships between relative humidity of exit air / H_2 and air stoichiometric number under different water removal from anode, the optimal temperature for the cell stable operation and membrane conductivity will be also established.

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CHAPTER 2 Literature Review**2.1 PEM fuel cell electrodes**

The gas diffusion electrode (GDE) in a PEMFC is a key component that affects the performance and cost of the fuel cell due to its noble metal Pt content. Improvement in the properties of electrode is the most practical way to increase fuel cell performance and decrease the cost of fuel cell. Typically, a GDE in a PEMFC structurally comprises a catalyst layer (CL) and a gas diffusion layer (GDL).

2.1.1 Catalyst layer

The catalyst layer must provide high activities for the electrochemical oxidation of fuels at the anode and reduction of oxygen at the cathode, and it must be stable to operate for tens of thousands of hours. Researchers over several decades have found that platinum and platinum-containing catalysts are the most effective catalyst material, in terms of both activity and stability. More recent efforts have been spent studying how to use platinum more effectively, which is determined by the total polarization losses associated with the rates of charge transfer at the catalyst-proton conductor-reactant gas (three) phase boundaries, the effective conductivity of proton conductor, and the rates of transport of gases through the porous catalyst layer.

The first generation of PEMFC electrode used PTFE-bound Pt black with loading of 4 mg cm^{-2} that has prohibitively high cost [Srinivasan et al, 1988]. A generous amount of research has been directed at reducing Pt loading below 0.4 mg cm^{-2} by using PTFE-bound carbon-supported nano-size Pt particles. Recently, platinum loadings as low as 0.1 mg cm^{-2} have been reported using Nafion-bound hydrophilic (thin-film) catalyst layer [Litster and McLean, 2004].

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2.1.1.1 Hydrophobic (PTFE-bound) catalyst layer

The hydrophobic PTFE-bound catalyst layer was developed for PEMFC employed in Gemini missions in the 1960's. Neidrach and Alford [1969] were credited with the introduction of PTFE-bound electrodes. Catalyst layer consists of Pt black or carbon supported Pt catalysts that are hydrophilic, blended with fine particles of hydrophobic PTFE. In these catalyst layers, the catalyst particles were bound by a hydrophobic PTFE structure commonly cast to the diffusion layer. This method was able to reduce the platinum loading of prior PEM fuel cells by a factor of 10; from 4 to 0.4 mg cm⁻² [Ticianelli et al., 1988]. Before fuel cell operation, some of the pores were filled with electrolyte while others are empty, a process called Nafion impregnation, thus providing a large vapor/liquid interfacial area and increasing the reaction interface leading to better catalyst utilization and performance. The interface is quite stable due to the high capillary forces that exist in small pores.

Lee et al. [1998] investigated the effect of Nafion impregnation on commercial low-platinum loading PEMFC electrodes. The researchers employed a conventional MEA with PTFE-bound catalyst layers featuring platinum loadings of 0.4 mg cm⁻². Nafion was impregnated in the electrode structures, with the Nafion loadings varying from 0 to 2.7 mg cm⁻², by a brushing method. The results presented by Lee et al. depict a non-linear relationship between the performance and the Nafion loading. In addition, the polarization curves showed that the O₂ content affects the optimum of Nafion loading. When the oxidant was air, there was a sharp increase in performance as the Nafion loading was increased to 0.6 mg cm⁻². However, performance dropped as additional Nafion was added. The researchers found that 0.6 mgcm⁻² was the ideal Nafion loading when operating on air. When pure oxygen was employed as the oxidant, the optimum Nafion loading was 1.9 mg cm⁻². This difference in the

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optimum Nafion loading was explained by the mass transport being the limiting rate when air is the oxidant, due to the low partial pressure of oxygen. Without the addition of some Nafion, the majority of the catalyst sites were inactive. However, if Nafion added is excess, the porosity of the composite decreases and limits mass transfer. The similar work also was done by Uchida et al. [1995] earlier than Lee et al. In their work, the optimal Nafion loading of 0.9 mg cm^{-2} was found in the dual-layer electrode with Pt loading of 0.5 mg cm^{-2} .

2.1.1.2 Hydrophilic (thin-film) catalyst layer

Wilson and Gottesfeld [1992] from US Los Alamos National Laboratory proposed a new structure for the Pt/C catalyst layer that substantially increased the utilization efficiency of the catalyst. Fabricating the catalyst layers and gas diffusion backings separately makes it possible to formulate each structure with the properties that are most suitable for its function. In the case of the catalyst layer, the optimal properties are hydrophilicity, thinness, uniformity, and the proper ratio of ionomer and supported catalyst. The catalyst layers are cast from solution as thin films that utilize the ionomer itself as a binder. The thin films are hot pressed directly onto the ionomer membranes, and the hydrophobic gas diffusion backings are inserted when the cells are assembled. In subsequent experiment done by Wilson et al. [1995], low platinum loading catalyst layers consist of a thin film of highly inter-mixed ionomer and catalyst that is applied to the electrolyte membrane. High performances are achieved with loadings as low as $0.12 \text{ mgPt cm}^{-2}$ at the cathode and even lower loadings are achieved at the anode. However, the long-term performance of these fuel cells depends upon the structural integrity of the recast, ionomer-bound catalyst layers.

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An Italian research group evaluated the influence of the Nafion content in gas diffusion electrodes with intermixed ionomer in the catalyst [Antolini et al., 1999, Passalacqua et al., 2001]. In their early study [Antolini et al., 1999]; the effect of Nafion loading was investigated on electrodes at 25 °C in 1.0 M H₂SO₄. In the study, an empirical equation ($Nafion \cong 56 \frac{L_{Pt}}{P_{Pt}}$, L_{Pt} is the platinum loading in the unit of mgcm⁻² and P_{Pt} the weight percentage of metal supported on carbon) for the estimation of the optimal Nafion loading in the catalyst layer was developed. The subsequent studies [Passalacqua et al., 2001] were carried out in a 50 cm² single cell in H₂/air operation at 70 °C. Low platinum loading (0.1 mg cm²) electrodes with a Nafion content ranging from 14 to 66 wt% were studied. The performance of PEMFC electrodes is affected by the Nafion content and an optimal content of about 33 wt% of ionomer was found.

Li and Pickup [2003] studied the effect of Nafion loading in the cathode catalyst layer by impedance spectroscopy, cyclic voltammetry, and polarization experiments. Catalyst utilization, determined by cyclic voltammetry, peaked at 76% for a Nafion loading of ca. 30 mass %, and this coincides with the optimum performance obtained in H₂/O₂ fuel cells. The impedance results show that the ionic conductivity of the cathode increased greatly with increasing Nafion content, and this is the main factor responsible for the increase in performance up to 30% Nafion. The loss of performance at higher Nafion loadings must have been due to an increasing oxygen transport resistance, because the electronic resistance did not increase significantly. In fact, the highest electronic resistances were observed at low Nafion loadings, indicating that Nafion played a significant role as a binder.

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Though many studies have been reported on the effect of Nafion content on electrode performance, best results have been reported at different Nafion loadings by different researchers. As the platinum loading increases, the electrode thickness and Nafion thickness grows and hence the optimum Nafion content may depend on the platinum loading. Sasikumar et al. [2004] examined the correlation of platinum loading and optimum Nafion content in the electrode and found that optimum Nafion requirement depends on the platinum loading and it increases with the decrease in Pt loading. For electrodes with 0.5, 0.25 and 0.1 mg cm⁻² Pt loading, best performance was obtained at about 20, 40 and 50% Nafion ionomer loading, respectively.

2.1.2 Gas diffusion layer (GDL)

The porous gas diffusion layer in PEM fuel cells ensures that reactants effectively diffuse to the catalyst layer. In addition, the gas diffusion layer is the electrical conductor that transports electrons to and from the catalyst layer. Typically, gas diffusion layers are constructed from porous carbon paper, or carbon cloth, with a thickness in the range of 100–300 µm. The gas diffusion layer also assists in water management by allowing an appropriate amount of water to reach, and be held at, the membrane for hydration. In addition, gas diffusion layers are typically wet-proofed with a PTFE (Teflon) coating to ensure that the pores of the gas diffusion layer do not become congested with liquid water.

2.1.2.1 Structure of GDL

Gas diffusion layer (GDL) is the critical component in achieving high performance in PEMFC. The requirements of an ideal GDL are several, including providing a physical support for the catalyst layer; effectively transporting the gas reactants to the catalyst layers; providing low electronic resistivity; having a surface that enhances good electronic contact; and having proper hydrophobicity for good water

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management in low temperature PEMFC. The GDL in the electrode is constructed from either a sheet of electrically conductive macro-porous substrate, such as a non-woven carbon paper or a woven carbon cloth, so called one-layer GDL and or with added a thin micro-porous layer (MPL) of carbon black mixed with polytetrafluoroethylene (PTFE) referred as dual-layer GDL. The one-layer GDL with macro-pores in its structure can efficiently transport the gas reactants to the catalyst layers, but provide a poor physical support for the catalyst layer for depositing catalyst particles which easily drop into its macro-structure when preparing the catalyst layer and a large contact resistance with catalyst layer [Jordan et al.,2000], in addition the macro-structure of one-layer GDL is unfavorable to water management in the cell [Wilson et al., Qi and Kaufman]. The dual-layer GDL with a MPL inserted between the catalyst layer and macro-substrate will overcome the disadvantages of one-layer GDL with functions: (1) to provide a physical micro-porous support for the catalyst layer; (2) to minimize electrical contact resistance with the adjacent catalyst layer, (3) to achieve a proper hydrophobicity in the adjacent catalyst layer for better water management and, (4) to prevent the catalyst layer ink from dropping into the electrode backing, thereby increasing the catalyst utilization. However, the introduction of MPL in the dual-layer GDL will increase the thickness with increasing the gas diffusion distance for mass transport, and MPL also provides more micro-pores in the structure (MPL will be easily compressed and tighten in the structure in the preparing process), which would cause increasing the tortuosity of the diffusion media to decrease the effective diffusion coefficient of the GDL. Thus, the dual-layer GDL will be confronted with a larger mass transport limitation than the one-layer GDL when a fuel cell is at higher current density. The other type of GDL is the carbon cloth with carbon/PTFE coating on both faces. As reported by Wilson et al.

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[1995], this kind of GDL (E-TEK backing) presented much higher limiting current density than that of one-layer carbon paper (Kherea paper), although mean pore sizes were 30 μm in the Kherea paper and $< 1 \mu\text{m}$ in the E-TEK backing. Higher performance with double-side coated cloth was probably due to higher in - plane gas permeability and less contact resistance between electrode and membrane / flow field plate. Antolini et al. used micro-porous diffusion layers with different PTFE onto the two sides of carbon cloth. They found that the micro-porous diffusion layers with 30% PTFE content on the gas side and 15% PTFE content on the catalyst side showed the best fuel cell performance. It was suggested that the higher PTFE content on the gas side facilitated gas transport and the lower PTFE content on the catalyst side increased electrode hydration level. However, the double-side carbon coated carbon cloth easily sunk into the flow field channel to block the gas flow.

Campbell et al. [1999] proposed a different type of GDL, which consisted of macro-porous substrates (which can be any poor electrically conductive or insulating materials) as the electrode backing and filled it with a mixture of an electrically conductive carbon powder and a hydrophobic polymer binder. In their study, a poor electrical conducting non-woven carbon fiber mat with 2.27 $\Omega \text{ cm}$ of through-plane resistivity (compared with 0.17 $\Omega \text{ cm}$ for conventional carbon fiber papers), a nonconductive glass fiber mat and an expanded PTFE mesh filled with a mixture of Shawinigan carbon and PTFE/FEP120 binder were used. The cell performance with this type of GDL was comparable with the conventional GDLs as mentioned above. The results revealed that the electrically conductive material, such as carbon, filled inside the macro-porous electrode backing is critical to the conductivity of the gas diffusion electrode, and this appears to provide the flexibility in the selection of various porous sheet materials for the electrode backing. Unfortunately, only a

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handful of studies on this type of GDL have been carried out so far. Furthermore, few published studies on this type of GDL using a carbon paper filled with carbon/PTFE filler have been presented.

2.1.2.2 Carbon loading and thickness

The carbon loading is equivalent to the thickness of the hydrophobic carbon layer. The higher the carbon loading, the thicker the hydrophobic carbon layer. The thickness of the diffusion layer was reported to have a much greater influence compared with the PTFE content by Paganin et al. [1996]. In their study diffusion layers of various thickness 15, 25, 35, 50, 65 μm inside carbon cloth were investigated, and a diffusion layer thickness of 50 μm was found to give the best performance, corresponding to a $\sim 25\%$ increase in maximum power density compared with the worst-performing 15 μm diffusion layer. They suggested that the effect of diffusion layer thickness was attributed to a decrease in the electrical resistance of the gas diffusion electrode as the diffusion layer thickness was increased. The decrease in the performance with the highest-loading 65 μm diffusion layer was attributed to a long gas diffusion path or with flooding problems. Jordan et al. [2000] studied the effect of carbon loading in the diffusion layer on the fuel cell performance. In their study diffusion layers with various carbon loading 0.7, 1.25, 1.9, 2.5 mg/cm^2 of Acetylene Black carbon on carbon paper were investigated. The optimal carbon loading 1.9 mg/cm^2 in the diffusion layer was found. Their results were consistent with the results reported by Paganin et al. [1996].

2.1.2.3 Polytetrafluoroethylene (PTFE) content

Antolini et al. [2002] suggested that the presence of PTFE in the gas diffusion layer serves three functions, binding the high surface carbon particles into a cohesive layer,

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forming gases transport channels and imparting some hydrophobic character to the layer. They investigated the effects on the fuel cell performance of different PTFE contents in the additional hydrophobic carbon layer on the cathode, and found that the best performance of the fuel cell at high current densities can be achieved by using the cathode with PTFE content of 30%. Paganin et al. [1996] have investigated the performance of PEMFCs containing Vulcan XC-72R carbon black diffusion layers with varying PTFE contents and diffusion layer thickness. The content of PTFE 10, 15, 20, 30, 40% in the diffusion layer was tested and found to have a small effect on the cell performance, a diffusion layer containing 15% PTFE giving the best performance. A possible explanation, given by Giorgi et al. [1998], is that the content of PTFE affects the porosity of the diffusion layer, an increase in the PTFE content resulting in a decrease in diffusion layer porosity. Lufrano et al. [1999] investigated the influence of PTFE content on the fuel cell performance, an optimum 20wt% PTFE content in the carbon layer has been found with Vulcan XC-72.

On the other hand, the introduction of the hydrophobic polymer (such as PTFE) into the structure of GDL could improve the water management in the GDL. The effect of PTFE on the performance and properties of GDL have been reported in a number of papers [Giorgi et al., 1998; Lim and Wang, 2004; Lin and Nguyen, 2005; Ioroi et al., 2003; Park et al., 2004; Qi and Kaufman, 2002; Jordan et al., 2000]. All of the studies are focused on the optimization of PTFE content in the single-layer (a macro-porous carbon paper as GDL) or dual-layer (a carbon paper with a micro-porous carbon/PTFE sub-layer) structures of GDLs, and the effect on porosity/pore size distribution and hydrophobicity of the GDL for understanding the mass transport of reactant gases/liquid product through the GDL. However, there are only handful of reports on the quantitative investigation effect of PTFE on the basic parameters such

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as the water saturation, the liquid volume fraction and gas volume fraction of the gas diffusion layer (GDL) for two-phase flow and transport in the GDL, and the effect of these parameters on the performance of PEMFC.

2.2 Nafion series H^+ membrane

The proton exchange membrane is the vital component of a PEM fuel cell, which makes it possible to attain high power densities. For optimum fuel cell performance it is crucial to keep the membrane fully humidified at all times, since the conductivity depends directly on the water content [Springer et al., 1991]. The thickness of the membrane is also important, since a thinner membrane reduces the ohmic losses in a cell. However, if the membrane is too thin, hydrogen, which is much more diffusive than oxygen, will be allowed to cross-over to the cathode side and recombine with the oxygen without providing electrons for the external circuit. Typically, the thickness of a membrane is in the range of 5 - 200 μm [Kerres, 2001]. The main requirement of polymeric membranes used in fuel cells includes: good mechanical, chemical and thermal strength and stability in the operating condition; extremely low permeability to reactant species to maximize coulombic efficiency; high proton conductivity to support high current with minimal resistive losses and zero electronic conductivity; production costs compatible with the application; and low swelling [Du, 2001].

Proton exchange membranes normally can be classified as, according to their fluorine content, perfluorinated (complete fluorinated), partially fluorinated, and non-fluorinated [Du, 2001]. However, perfluorinated polymer electrolyte is most commonly used. The most well known and well established of perfluorinated polymer is Nafion, E.I. DuPont de Nemours and Co. This material usually used 'standard' electrolyte against which others are judged. Other commercially available

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perfluorinated ionomer membranes include Aciplex (Asahi Chemical Industry Co., Ltd.), Flemion (Asahi Glass Co., Ltd), and Dow (Dow Chemical Co.) membranes.

Nafion membrane consists of three regions: (1) a polytetrafluoroethylene (PTFE, a.k.a. DuPont's TeflonTM) – as backbone; (2) side chains of $-O-CF_2-CF-O-$ $-CF_2-CF_2-$ which connect the molecular backbone to third region; and (3) ion clusters consisting of sulfonic acid ions SO_3H^+ . The negative ions, SO_3^- , are permanently attached to the side chain and cannot move. When the membrane becomes hydrated, the hydrogen ions in the third region become mobile by bonding to the water molecules and hopping from SO_3^- site to SO_3^- site within the membrane. Because of this mechanism, the hydrated Nafion-based electrolyte is an excellent conductor of hydrogen ions. Normally, the proton conductivity of hydrated Nafion membranes dramatically increases with water content and reaches values of 0.1 to 0.2 $S\ cm^{-1}$ at 25 – 80 °C [Rikukawa et al., 2000].

The challenges with polymer electrolyte membrane have been and still are their temperature limitation and high cost ($US\$700\ m^{-2}$) [Lufrano et al., 2000; Costamagna and Srinivasan, 2001]. PEM fuel cells are limited by the temperature range over which water is a liquid. Basically, the operation of PEM fuel cells at elevated temperatures increases the rates of reaction, reduces problems related to catalyst poisoning by absorbed carbon monoxide in the 150-200 °C range, reduces the loading of expensive Pt and Pt alloy catalysts, and minimizes problems due to electrode flooding [Rikukawa et al., 2000]. However, PEM such as Nafion is opt to be dehydrated at the temperature above the boiling point of water, and thus the proton conductivity of the dehydrated membrane is significantly reduced. The PEM membrane must be kept hydrated to retain proton conductivity. Thus, the operating

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temperature for normal PEM must be kept below the boiling point of water. Operating polymer electrolyte membrane fuel cells at temperatures exceeding 100 °C is possible under pressurized conditions. High pressure is required to keep the water in a liquid state, but shortens the life of the membrane. To develop a high-temperature membrane for fuel cell applications, one approach is to modify a Nafion membrane by embedding a second substance such as nano-sized SiO₂ / TiO₂, which could retain water at higher temperature [Wainright et al., 2003]. Several studies by Princeton University [Yang et al., 2001; Adjemian et al., 2002; Costamagna et al., 2002] reported high-performance MEAs based on composite membranes of Nafion hybridized with silica, alumina, titanium dioxide, and zirconium phosphates. The composite membranes gave cell performance of 0.65-0.7 V at 120°C, 0.58-0.66 V at 130°C, and 0.35-0.45 V at 140°C. Those membranes showed stable behavior during time when maintained at 130 °C, while irreversible degradation affected Nafion under the same conditions. However, all were operated at near fully humidified conditions, pressurized to 3 atm, and used neat oxygen.

So far, only perfluorinated proton exchange membranes are used in fuel cell systems, but high cost of Nafion membranes produced by DuPont Company results in high cost of PEMFC systems, which is one of the major factors affecting PEM fuel cell commercialization. Consequently, there is a demand for novel and alternative thermally and chemically stable polymer electrolytes combining the membrane properties of perfluorinated polyelectrolytes with lower cost and improved processability. To produce alternative membranes (non-fluorinated) materials which are cheaper than PFSA has become a highlighted R&D field. Some sacrifice in material lifetime and mechanical properties may be acceptable, providing the cost factors are commercially realistic [Rikukawa et al., 2000].

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2.3 Water management in PEM fuel cell

Membranes in PEM fuel cells are generally water filled to keep the conductivity high [Kordesh and Simader, 1996]; a dry membrane possesses a lower conductivity. Water management of the membrane is one of the major issues in PEM technology. A fully saturated membrane without containing too much excess water in the fuel cell is the main goal of water management. This ensures that the membrane is most conductive and that the fuel cell operates efficiently. In practice the membrane is not always fully saturated and thus it losses conductivity, typically at high current density.

2.3.1 Water transport in the membrane

Basically, the process of water transport in the membrane involves two pathways as shown in Fig.2-1. One is that the water is transported along with protons through the membrane from the anode to the cathode by the electro-osmotic drag which increases with increasing current density and humidity. The other is that the back-diffusion of water molecules from the cathode to the anode due to the concentration gradient which is built up by water produced at the cathode and the drive of electro-osmotic drag.

Fig. 2- 1 The schematic of water transport process in PEM fuel cell

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Contributing factors to water transport in the membrane are the water electro-osmotic drag through the cell - for every proton, and back diffusion from the cathode. The water balance in the membrane is related to the current density, the flow rate and humidity of the inlet gases, and the characteristics of membrane and electrodes. The water electro-osmotic drag is the process that protons migrate through the membrane from the anode to the cathode, carrying water molecules with them. The number of water molecules dragged with each proton is between 1 (gas vapor equilibrated membranes) and 2.5 (liquid water equilibrated membranes) [Fuller and Newman, 1992; Zawodzinski et al., 1995; Ise et al., 1999]. The water drag from the anode to the cathode is proportional to proton flow and thus this phenomenon increases with current density. The production of water at the cathode results in a gradient in the water activity across the PEM membrane. This gradient will result in the back diffusion of water from the cathode to the anode. The water diffusion coefficient has been typically measured by water-flux measurement. Nguyen and White [1993] derived an expression for the Fickian diffusion coefficient of water in Nafion, based on fuel cell performance data in the literature and the electro-osmotic drag measurements of Springer et al. [1991]. As a function of water content, the diffusion coefficient is expected to decrease as the water content decreases because the water is more tightly associated with the sulfonic acid sites. Motupally et al. [2000] measured the water diffusion coefficient by the water flux method. They found that the diffusion of water across Nafion membranes was a function of the water activity gradient using experimental data. The gradient in the activity of water across the membrane was varied by changing the flow rate and pressure of nitrogen gas on one side of the membrane. Experimental studies on water transport in working fuel cells have been mainly investigated by measurements [Jansen and Overvelde, 2001; Sena

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et al., 1999; Yan et al., 2006]. Jansen and Overvelde [2001] examined the water transport in the proton-exchange-membrane fuel cell by measurements of the effective drag coefficient. It was found that the humidity and the stoichiometry of the inlet gases had a large effect on the effective drag, the effective drag did not depend significantly on the current density (at fixed stoichiometry), and the net electro-osmotic drag coefficient through the membrane can be negative (-0.16 when using dry reactants at both anode and cathode). The membrane thickness was also found to be the most significant parameter, which affected the net electro-osmotic drag coefficient. Sena et al. [1999] examined the effect of water transport in a PEMFC at low temperatures operating with dry hydrogen. In their work, an experimental study of the polarization response of a H_2/O_2 PEMFC was carried out at low temperatures as a function of the membrane thickness. Yan et al. [2006] also determined water balance in a polymer electrolyte membrane fuel cell (PEMFC) by measurements of the net drag coefficient under various conditions. In their work, it was found that the net drag coefficient (net number of water molecules transported per proton) ranged from -0.02 to 0.93, and was dependent on the operating conditions, the current load and the level of humidification.

As mentioned above, the water management in the membrane is dependant on several factors, such as the current density, the flow rate and humidity of the inlet gases, and the characteristics of membrane and electrodes. Therefore, it is not easy to keep the entire membrane hydrated properly, especially, at high current densities. To combat water management problems, the humidification techniques are applied to PME fuel cell. One way is to humidify the reactants gases entering the fuel cell by adding water vapor, which is more suitable for a single cell operation, but complicated for a fuel cell stack. The other way is to use self-humidifying membranes, which are made by

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impregnating a Nafion membrane with a few weight-percentage of SiO_2 or TiO_2 . The water forms at the cathode and the water transported by electro-osmotic drag are adsorbed by the oxide particles, to ensure hydration of the membrane at all times. The cell is very stable and a high performance is obtained even under ambient conditions [Watanabe et al., 1996].

Fig. 2- 2 The schematic diagram of self-humidifying membrane developed by Watanabe et al. [1996]

2.3.2 Self-humidification

Watanabe et al. [1996] first developed a self-humidifying membrane by recasting the solubilized Nafion ionomer and incorporating in it with nano-sized Pt and metal oxide particles as shown in Fig.2-2. The nano-sized particles of Pt and oxides such as TiO_2 or SiO_2 were highly dispersed in the thin electrolyte membranes. The platinum and added oxides provide a means for combining H_2 and O_2 into water, thus retaining the water on the hygroscopic oxides to maintain the water content in membrane. The cell using the self-humidifying membrane reported by the researchers showed stable and high performance even under ambient pressure conditions when operated with hydrogen saturated with water at 20°C and dry oxygen. The output of the cell reached 0.63 W cm^{-2} at 0.9 A cm^{-2} with 0.7 V . In order to clarify the self-humidifying

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properties in the Pt-PEM, the amount of water vapor produced by the recombination and the faradaic reaction was analyzed together with those of consumed H_2 and O_2 by monitoring humidity in the exhausting gases from PEMFCs operated with dry H_2 and O_2 [Watanabe et al. 1998]. The H_2 used for the self-humidification increased with increasing output current density, but the total H_2 consumption decreased to ca. 2/3 of that in normal membranes. All H_2O produced inside the Pt-PEM was found to be exhausted from the anode, resulting in the efficient humidification of the membrane on the anode side, which is dried by electro-osmotic drag. Thus, the resistance of the Pt-PEM was lowered to $0.04 \Omega \text{ cm}^2$. It was also found that the Pt-PEM improved the cathode potential distinctively, which was ascribed to elimination of the chemical reaction of crossover gases in the cathode catalyst layer, and eliminated any disturbance of O_2 diffusion by water vapor produced by the reaction. In their subsequent works [Uchida et al., 2003], the preparation method of TiO_2 nanoparticles in a commercial Nafion 112 membrane via in situ sol-gel reactions was developed, resulting in a transparent membrane with uniform distribution of TiO_2 in the PEM. Water adsorbability increased more than two times by dispersing only 2 wt % TiO_2 in the PEM. That newly prepared TiO_2 -PEM cooperated with highly dispersed Pt nanoparticles $\sim$ Pt- TiO_2 -PEM was confirmed to perform a self-humidifying operation in a PEMFC with dry H_2 and O_2 . In their most recent study [Hagihara et al. 2006], they have developed preparation method of practically large size self-humidifying polymer electrolyte membranes with highly dispersed nanometer-sized Pt and/or SiO_2 for fuel cells. The Pt particles were expected to catalyze the recombination of H_2 and O_2 , leading to a suppression of the chemical short-circuit reaction at the electrodes, while the SiO_2 particles were expected to adsorb the water produced at the Pt particles together with that produced at the cathode reaction. Stable SiO_2 particles were formed

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in a commercial PEM (Nafion[®] 112) via in situ sol–gel reactions at 70 °C. It was found by SAXS that the hydrophilic cluster size increased by water adsorbed SiO₂, which may contribute to the increase in the proton conductivity due to the adsorbed water by SiO₂. Pt particles were uniformly dispersed in a Na⁺-form normal-PEM or SiO₂-PEM by an ion-exchange reaction with [Pt(NH₃)₄]Cl₂, followed by a reduction with 1-pentanol at 125 °C. The newly prepared Pt-SiO₂-PEM was found to perform a self-humidifying operation in a standard-size PEMFC (25 cm² electrode area) with H₂ and O₂ humidified at 30 °C. The performance of the Pt-SiO₂-PEM cell operated with the low humidity reactant gases was as high as the normal-PEM cell fully humidified, because the ohmic resistance of the former cell was not affected by the incorporation of Pt – SiO₂ nano-particles.

There are also other research groups to study self-humidify membrane using different fabrication methods [Yang et al. 2002; Liu et al. 2003; Xing et al. 2004, and Yang et al. 2005;]. For example, a Korea group [Yang et al. 2002] developed a new preparation method that involved the fabrication of a sandwich structure, which is comprised of two membranes made of perfluorosulfonylfluoride copolymer resin and fine Pt particles lying between them, coated by sputtering. The optimum pre-forming temperature for the pore-free membrane sheet is determined to be 230 °C, based upon the results of successive experiments. A Chinese group [Liu et al. 2003] reported a novel preparation method for self-humidifying membranes. Using solution-cast method, PTFE porous substrates in these composite membranes increased the strength and distribute self-humidifying layers adjacent to the anode side. Compared with the cells fabricated with ordinary membranes, the performance of the cells with these self-humidifying proton exchange membranes are dramatically improved in both cell voltage and the current density under dry conditions, and the cell using the

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Pt/C-PEM shows the best and most stable performance. A US group [Chalkova et al. 2005] prepared the composite membranes using a recast procedure that showed a pronounced improvement over unmodified Nafion membranes when operated at 120 °C and reduced relative humidity (RH). For instance, at 50% RH, the Nafion/20% TiO₂ membrane demonstrated a performance identical to that of an unmodified Nafion membrane operated at 100% RH using H₂/O₂ as reactants. This performance level was comparable to that of a bare Nafion membrane at 80 °C. The high performance of the Nafion/TiO₂ composite membranes at low RH was attributed to the improved water retention due to the presence of absorbed water on the TiO₂ surface.

Several modeling studies and experimental results expounded that PEM fuel cell operation with internal humidification from the water generated by electrochemical reaction and the self-water balance in membrane is feasible at a restricted operating condition with regard to gas flow rates and cell temperature or specific electrode/flow field design. For example, Büchi and Srinivasan [1997] developed a model for the prediction of the possibility of operating a PEM fuel cell without external humidification of the gases and experimentally verified the model. In their experiment, a PEM fuel cell with conventional MEA using Nafion 115 demonstrated stable long-term operation over a period of 1800 h at the temperature of cell up to 60 °C with dry reactant gases. However, it was also found that the unhumidified cell still performed 20 to 40% of current density at 0.6 V lower than an identical cell with humidified reactants even if the air flow rate and temperature were correctly set. Qi et al. [2002] designed a double-path-type flow-field that has two gas inlets and two gas outlets. The two paths were arranged in such a way that the inlet of one flow-field is adjacent to the outlet of the other flow-field and, within any section of the electrode

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active area, there are always adjacent channels with reactant flowing in opposite directions. Such a design enables the dry entering gas to become hydrated by acquiring some moisture from the exiting moist gas; and, within any section of the active area, the drier gas in one flow-field can share the moisture in the wetter gas flowing in the other flow-field. Such a design effectively uses the water produced by the stack to hydrate the membrane and the catalyst layers. The effectiveness of this design was demonstrated by running multiple-cell stacks where the stack could run stably at a current density up to 0.33 A/cm^2 using dry hydrogen and dry air. Recently, Ge et al. [2005] used a water-absorbing sponge made of polyvinyl alcohol to develop an internally humidified system. The water sponge was advantageous for humidification of the dry inlet air and for removal of liquid water from the cell.

2.3.3 Liquid water transport in GDL

GDL is an essential component of PEMFCs. It serves as a support for the polymer electrolyte membrane, distributes reactant gas over the catalyst layer, and conducts electrons from reaction sites to the outer circuit. At high current densities, the electrochemical reaction rate is faster than the amount of reactants supplied, specifically oxidizer; therefore, the reaction rate is limited by the transport rate of oxidizer to the reaction sites, which is sandwiched between GDL and PEM. In addition, when the liquid water blocks some pores of GDL, the reactant transport is further limited. As such, GDL for PEMFC is commonly Teflon-treated to provide highly hydrophobic surface for easy removal of liquid water. When water vapor pressure exceeds the saturation level, condensation starts, forming a tree-like liquid water percolation in the porous GDL as shown in Fig.2-4(a) [Nam and Kaviany, 2003; Pasaogullari and Wang 2004]. The liquid water reaches the interface of porous GDL and open channel, forming liquid droplets. Nam and Kaviany [2003] has verified the

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large water droplet formed at the interface of macro-porous GDL by environmental scanning electron micrographs (ESEM) as shown in Fig 2-3. First, the liquid water has formed as droplets instead of a film. As well, it can be seen that over time, with greater levels of liquid water present, the droplets have connected and traveled toward areas of greater liquid accumulation. It is apparent that over 50% open space of the GDL is covered with liquid water, which would reduce the access of oxygen from the flow field to the catalyst layer to decrease the cell performance, especially at high current density.

Fig. 2- 3 The large water droplet formed at the interface of macro-porous GDL by environmental scanning electron micrographs (ESEM) (Nam and Kaviany, 2003)

Inside GDL, liquid water is driven by capillary action. This capillary action is a result of capillary pressure distribution, which is defined as the difference between gas and liquid-phase pressures. In hydrophobic GDL, the capillary pressure is negative; hence, the liquid pressure is larger than the gas-phase pressure, whereas in hydrophilic media, the gas-phase pressure is higher than that of the liquid phase. In addition, the liquid pressure increases with the fraction of void spaces occupied by liquid water; therefore, a liquid pressure gradient is formed from higher to lower liquid saturation regions. This pressure gradient becomes the driving force for liquid water flow. The liquid saturation is higher at the catalyst layer, due to water generation and electro-osmotic

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drag, than the GDL-channel interface. Therefore, the liquid pressure gradient formed in the GDL drives liquid water from the reaction sites toward the open channel [Pasaogullari and Wang 2004]. Lister et al [2005] presented that the water transport is dominated by fingering and channeling and features numerous “dead ends”, where water transport recedes when an adjacent breakthrough channel forms, after the liquid has broken through a constriction it is seen to fill the entire void space surrounded by other fiber cross-sections as shown in Fig.2-4(b).

Fig. 2- 4 Water transport processes in hydrophobic GDL of PEMFC proposed by (a) Nam and Kaviani [2003], and Pasaogullari and Wang [2004] (b) Lister and Dijlali [2005]

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3.1 Membrane electrode assembly (MEA) fabrication

3.1.1 Electrode preparation

3.1.1.1 Preparation of a wet-proofed electrode backing

Commercial available carbon papers, such as PE-704 carbon paper (SGL, SIGRATHERM[®] paper) and TGP-H-030 carbon paper (Toray carbon papers) were used as electrode backing materials. Prior to the preparation of gas diffusion layer (GDL), the carbon papers must be hydrophobic-treated with polytetrafluoroethylene (PTFE) to strengthen the structure of the carbon paper and increase the hydrophobicity of the carbon paper. The PTFE emulsion (60 wt.%, Aldrich) was first diluted with deionized water (the mass ratio of 60% PTFE to deionized water is 1:10) to form a diluted PTFE emulsion to reduce the dead pores in carbon paper when treated. The carbon paper was then repeatedly impregnated with the diluted PTFE emulsion followed by drying at 120 °C until the weight of carbon paper was increased by 40%; it was further heated at 240 °C for 0.5 hr to remove the dispersant containing the PTFE and finally sintered at 340 °C for 0.5 hr. The wet-proofed carbon paper can be directly used as one-layer GDL.

3.1.1.2 Preparation of gas diffusion layer

The hydrophobic-treated carbon paper was coated a micro-porous layer (MPL) on one side with a mixture of carbon powder and PTFE polymer to form dual-layer GDL, and whole-structurally filled with a mixture of carbon powder and PTFE polymer to form carbon-filled gas diffusion layer (CFGDL). Vulcan XC-72 carbon powder (Cabot Co.) was used as the electrically conductive filler and PTFE (60 wt. %, Aldrich) was used as the binder. A paste composed of carbon powder and PTFE was

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prepared by dispersing Vulcan XC-72 carbon powder into anhydrous ethanol (the mass ratio of carbon powder to ethanol is 1:20) in an ultrasonic tank with a frequency of 25 kHz followed by adding PTFE emulsion into the dispersion drop by drop under gently stirring. Afterwards, the paste was pressed into the PTFE treated carbon paper to form the CFGDL by brushing and the thickness of the composite structure was maintained the same as that of the carbon paper. To prepare dual-layer GDL, the paste was sprayed onto the PTFE treated carbon paper to form a MPL and the thickness of MPL was dependent on the carbon loading. These composite structures were finally dried and sintered at 340 °C for 1 hr for making the catalyst layer. The loading of carbon / PTFE on a GDL was controlled by the enhanced weight of the GDL. The variance between the expected loading and actual loading on different sample types (15cm X 20cm in dimension) is less than 2%.

3.1.1.3 Preparation of catalyst layer

To prepare the hydrophobic catalyst layer, a homogeneous dispersion of catalyst in isopropanol (the mass ratio of carbon powder to ethanol is 1:20) - catalyst paste – was prepared with the E-TEK 20 wt.% Pt/C catalyst and 60% PTFE emulsion in the same procedure as preparation of the paste for making GDL as mentioned above. The mass ratio of catalyst (E-TEK 20 wt.% Pt/C) to PTFE (60 wt.%, Aldrich) was 2:1. The catalyst paste was then applied onto one side of GDL by using a painting method. The electrode was finally dried and sintered at 340 °C under inert gas environment for 0.5 hr. Both the anode and cathode were prepared in the same manner. The Pt loading on the electrode was 0.4 mgcm⁻². For the extension of the three-phase interface zone in the catalyst layer [Raistrick, 1989; Srinivasan et al., 1988], this kind of electrode was protonated with Nafion solution (5112 from DuPont) before making membrane electrode assembly (MEA). The procedure includes: (1) diluting 5 % Nafion (from

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DuPont) 3 – 5 fold with isopropanol; (2) spraying the diluting Nafion solution onto the surface of the catalyst layer of hydrophobic electrode by a airbrush with a nozzle diameter of 0.3 mm (Model HP-102, Olympos Co. Ltd.) at the pressure 0.5 bar; (3) drying the protonated electrode in a vacuum oven at 80 °C for 1 hr. The dry loading of Nafion on the electrode was approximately 1 mgcm⁻².

To making hydrophilic catalyst layer, a homogeneous suspension was formed from the E-TEK 20 wt.% Pt/C catalyst, 5% Nafion solution with ethanol/isopropanol mixture as solvent and glycerol in an ultrasonic tank with a frequency of 25 kHz. The resulting ink was coated onto the GDL by a brushing procedure to produce a thin catalyst layer (thickness less than 50 µm). Platinum loading on the electrode is 0.4 mgcm⁻². Finally, the electrodes were heat-treated in a vacuum oven at 150 °C for 1 hr. The same can be done for electrode. The catalyst loading on the electrode was controlled by the enhanced weight of the electrode. The deviation between the expected catalyst loading and actual loading of an electrode (15cm X 20cm in dimension) is less than 2%.

3.1.2 Pre-treatment of proton exchange membrane

Nafion series membranes (N117, N115, N1135, N112 and N111) were used for this study. This kind of membrane must be subjected to pretreatment to remove impurities and various kinds of cations before use [Ticianelli et al., 1988; Murphy et al., 1994]. The membranes were treated according to the conventional procedure of 1 hr in a 5 wt% solution of hydrogen peroxide at 80 °C, washed with deionized water for 3 – 5 times, 1 hr in 0.5 molL⁻¹ sulphuric acid at 80 °C, rinsed several 3 times with hot deionized water. The membranes were stored in the deionized water prior to use.

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3.1.3 MEA preparation

A pair of protonated electrodes (anode and cathode) was bonded onto both sides of purified proton-exchange membranes; using a hot-pressing procedure at 130 – 140 °C and 50 kg/cm² for 2 min. The hot-pressed MEA was immediately removed from the hot press machine and cooled in a cooling cell fixture to the room temperature.

The performance reproducibility of MEAs with the same materials prepared in this laboratory has been evaluated by a 5-cell stack with a cell active area of 20 cm². The variance in the potential of unit cell at a constant current density for the stack is less than ± 10 mV at a cell potential of 0.6 V.

3.2 Characterization of steady state polarization in PEM single cell

3.2.1 Cell fixture

A single cell was used to evaluate the performances of MEA components. This provides the opportunity for conducting steady state polarization measurements as well as cyclic voltammetry measurements for same membrane electrode assembly. The construction of single cell is schematically shown in Fig.3-1. A single cell was composed of end plates with stainless steel meshes, MEA, and sealing gasket (silicon rubber plate, 0.6 mm in thickness) which matches a pair of electrodes (anode and cathode) in thickness. The technique of single-gasket sealing was applied for all the testing cells. The percentage of gasket compression was about 0.17 (i.e., a gasket is compressed from 0.6 mm to 0.5 mm). The end plates played roles not only in fixing cell but also collecting electrical current, as did stainless steel meshes. The spaces in the stainless steel meshes between end plates and electrodes constituted the anode and cathode chambers, so called flow fields.

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Fig. 3- 1Schematic of a Single PEM fuel cell: (1, 6) Anode & cathode endplates; (2) hole for measuring temperature; (4) gaskets; (5) MEA; and (1, 3) end plate and flow fields

3.2.2 Cell test system

The single cell test system is schematically shown in Fig.3-2, which is equipped with gas sources, single cell, reactant humidifiers, refrigerated bath (LTD6G) for temperature control, pressure control, and flow control. The performance determination of single cell was carried out using Arbin electronic load and a personal computer with MITS software for a data acquisition/control.

The fuel cell measurement accuracy is mainly dependent on the operating conditions (cell temperature, reactant pressure and gas flow rate etc.). The cell operating temperature has a significantly influence on electrode performance under both external humidification and self-humidification. An increase in temperature lowers the internal resistance of a cell, mainly by increasing the proton conductivity of the electrolyte membrane under fully humidifying condition; On the other hand, an increase in temperature also increases the internal resistance of a cell, mainly by decreasing the proton conductivity of the electrolyte membrane under incompletely humidifying or self-humidifying conditions. For this reason, LTD6G refrigerated water bath with a high accuracy (its stability is ± 0.01 °C) was used in this work to

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control the operating temperature of fuel cell in the experiments to reduce the measurement error caused by temperature. Operating pressure also impacts electrode performance. A PEM fuel cell at 80 °C and 431 mA/cm² showed a voltage gain of 22 mV for the pressure increase from 2.4 bar to 3.4 bar [EG&G Services, 2000, 3-10]. Therefore, the “USG” two-stage pressure regulator (its accuracy is ± 0.1 bar), which is a high quality pressure regulator with *constant pressure* delivery with widely varying inlet pressures, was used in this work to control the air operating pressure. The flow rate for all the fuel cell testing was controlled by a fine regulator and calibrated with Gilibrator Air Flow Calibration System (1 – 250 ml/min and accuracy > 99%, Scientific Instrument Services, Inc.).

Fig. 3- 2 Schematic diagram of a single cell test system

3.2.3 Cell operating conditions

In an operating cell, water is produced at the cathode. If the rate of back diffusion of water from the cathode to the anode can not keep up with that of electrosmotic drag from the anode to the cathode, the membrane on the anode side would be dried out [Mosdale & Srinivasan, 1995]. Thus, an appropriate humidification for reactants is

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necessary to achieve a high and stable fuel cell performance. As seen in Fig.3-2, a conventional water-bubbled humidifier was used in the test system. In this kind of humidifier, the gas is bubbled through a water bath, and the gas humidity can be changed by varying the temperature. In this study, the humidification strategies were dependent on the purposes of experiments. When using H_2 and O_2 as reactants, an external humidification was only used to anode side (H_2). The temperature of humidification for H_2 gas was maintained as the same as the cell temperature. Flow direction on the anode and cathode used counter-flow pattern. The gas flow rates were kept at a fixed stoichiometry (1.15 times stoichiometric for H_2 and 2 times stoichiometric for O_2) at 1 A/cm^2 current density. Cell potential vs. current density measurement was conducted using H_2/O_2 of 1.5 bars in the range of 50-80 $^{\circ}\text{C}$.

When using H_2 /Air as reactants in an experiment, both H_2 and air were humidified with external humidifiers. The temperature of humidification has been maintained 5 $^{\circ}\text{C}$ higher than the cell temperature for H_2 and 5 $^{\circ}\text{C}$ lower than the cell temperature for air. Flow directions on the anode and cathode used co-flow pattern. The gas flow rates kept a fixed stoichiometry (1.15 times stoichiometric for H_2 and 2.5 times stoichiometric for air) at 1 A/cm^2 current density. Cell potential vs. current density measurement was conducted using H_2 /Air of 1.5 bars in the range of 50-80 $^{\circ}\text{C}$.

The same test procedure was used for single cells in comparative measurement between different sample types. All the fuel cells before testing were first active-treated / conditioned for about 5 hours at 55 $^{\circ}\text{C}$ / 50 $^{\circ}\text{C}$ / 50 $^{\circ}\text{C}$ ($T_{\text{anode humidifier}}$ / T_{cell} / $T_{\text{cathode humidifier}}$) at atmospheric pressures in the circuit shortcut. After the active-treated, the cells were used for various performance measurements.

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3.3 Physico-chemical Characterizations

3.3.1 Resistivity measurement for GDL

The through-plane resistivity of the GDL was measured by using a single cell fixture [D. Bevers et al., 1996] as shown in Fig.3-3. A GDL with an area of 5 cm² was assembled in the single cell fixture. A current was passed through the GDL and the voltage drop across the GDL sample was measured. The area specific resistance can be obtained from the linear slope of the $V-I$ curves and the through-plane resistivity, ρ_T , can thus be calculated using following equation:

$$\rho_T = \frac{R_{ASR,T}}{L}, \quad (3-1)$$

where $R_{ASR,T}$ is the area specific resistance measured and L is the thickness of the sample. Five pieces of each type sample were tested for the measurement. The mean value of the pieces of sample tested was used to plot figures. To assure that the tested GDLs would present similar electrical property, they were cut from the same sheet of GDL material (weight tolerance is less than $\pm 2\%$ with the area of 5 cm²). The measurement was carried out at room temperature (25 °C).

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Fig. 3- 3 Schematic diagram for the measurement of the through-plane resistivity of the GDL using a standard single cell fixture

3.3.2 Determination of electrochemically active surface area (ESA)

The cyclic voltammetric technique is used to estimate the electrochemically active surface areas (*ESA*) of Pt/C catalyst in the gas diffusion electrode of fuel cell. This technique can indirectly investigate the effects of electrode materials (such as carbon, PTFE, Nafion and other materials like hygroscopic oxide, silica), electrode structure and morphology on *ESA* of Pt/C catalyst. Figure (3-4) shows a typical CV with a description of various peaks in the curve, which can be described as three fundamental processes: (1) double layer charging, (2) hydrogen evolution at ~ 0 V and oxygen evolution ~ 1.5 V and (3) adsorption/desorption of H atoms ~ 0.05 - 0.3 V and the formation (>0.8 V) and reduction of Pt oxides (0.6 - 1.2 V). The *ESA* of gas diffusion electrode is evaluated from the voltammetric curves by assuming the value of $210 \mu\text{C}/\text{cm}^2$ for the hydrogen desorption charge on the smooth Pt [Ticianelli et al., 1988]. The coulombic charges for hydrogen desorption Q_H are calculated by subtracting the anodic “double-layer” charge from the total charge in the hydrogen desorption region. The electrochemical surface area (*ESA*) can be estimated from the following equation

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$$ESA(m^2/g) = \frac{(Q_H mC/cm^2 \text{ of } GA)(1000 \mu C/mC)}{(210 \mu C/cm^2)(10^4 cm^2/m^2) \times (w_{Pt} mg/cm^2 \text{ of } GA)(10^{-3} g/mg)}, \quad (3-2)$$

where, GA is the geometric area of electrode and w_{Pt} is Pt loading on the electrode.

Princeton Applied Research Potentiostat/galvanostat (Model/263A) was used for CV measurement. The investigated electrodes were the ones after the steady-state polarization measurement of fuel cells. In the measurement, humidified argon (Ar) was passed through the working electrode compartment (cathode) and humidified hydrogen (H_2) through the counter electrode compartment (anode). Because of the negligible overpotential at the counter electrode for H_2 oxidation or evolution reaction, the counter electrode also served as a reference electrode. The sweep rate in the measurements was 50 mV/s with a potential range of 0 ~ 1.5 V.

Fig. 3- 4 Cyclic Voltammogram of a fuel cell electrode

3.3.3 Electrochemical impedance spectroscopy (EIS)

EIS for characterization of fuel cell was conducted using a potentiostat-galvanostat Autolab FRA controlled by a personal computer. A single cell with the active area of

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1.5-cm² was used in the experiment. The working electrode was connected to the cathode; the counter and reference electrodes were linked to the anode. Impedance spectra were obtained at frequencies between 10 kHz and 0.01 Hz, and the ac signal amplitude was 10 mV rms.

The measurements of proton conductivity were carried out on Nafion-silica composite films with different silica contents sandwiched between two Pt disk probes at room temperature in the frequency range 0.01 – 100 kHz. The potentiostat/galvanostat (model 273, EG&G) equipped with a lock-in amplifier (model 5210, EG&G) was used in this experiment. The films resistance was obtained by extrapolating the impedance data to the real axis on the high frequency side (the impedance data were corrected for the contribution of the blank and short-circuited cell).

3.3.4 Microstructure and morphology characterization

3.3.4.1 Micro-structure observation by scanning electron microscope (SEM)/energy dispersive spectroscopy (EDS)

The morphological characteristics of the carbon paper with / without a hydrophobic polymer (PTFE), and gas diffusion layers (GDLs) with different structures were observed under scanning electron microscopy (SEM) (JSM-5600, JEOL, Japan). The cross section surface of samples was mechanically fractured after immersion in liquid nitrogen for the SEM observation. SEM provided the real images of surface structure and cross-section structure of the carbon paper and GDLs in this study to obtain the information of the surface roughness and thickness of the samples. The compositions on the surface of samples were obtained using the SEM equipped with EDS.

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3.3.4.2 Nano-structure observation by Field-emission scanning electron microscope (FESEM)

The high-resolution reached by FESEM (~ 2 nm) allows the study of the micro-structure in detail. By the use of FESEM (JSM-6700F, JEOL, Japan), the images of nano-structural particles (Pt/C catalyst, Pt particle on the carbon, Nafion, PTFE and hygroscopic oxides) distribution in the catalyst layer of electrode and micro-structure of catalyst layer can be clearly obtained. It is very useful to analyze the features of the porous electrode.

3.3.4.3 Nano-structure observation by Transmission electron microscope (TEM)

The nano-particles of Nafion, Pt/C catalyst, and silica were examined by a transmission electron microscope (TEM) (JEM 2010, JEOL). The sample was prepared by immersing copper grid coated with the suspension contained the investigated particle and then was allowed to dry at the room temperature. To observe the distribution of the nano-particles (Pt/C catalyst and silica) dispersed in the Nafion solution, the Nafion – Pt/C catalyst or Nafion – silica suspension was prepared from a 5% Nafion solution combined with alcohol and water, and then thoroughly mixed in an ultrasonic tank with a frequency of 25 kHz followed by drying out on copper grids for direct observation.

3.3.5 Mercury intrusion porosimetry

Pore size and distribution of the GDL were measured by a Mercury intrusion porosimetry (Autopore III 9420, Micromeritics Inc.). Mercury is a non-wetting liquid to most solid, but it can intrude the pores under pressure. The pore volume is the volume of the intruded liquid, and the pore size is related to pressure, which is expressed by the Washburn equation [Diamond, 2000]:

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$$d = -\frac{4\sigma \cos \theta}{P} \quad (3-3)$$

where d 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.

3.3.6 Water uptake measurement

3.3.6.1 Water uptake measurement of GDL

The wetting properties of the GDL as a function of PTFE content was measured by the water uptake. The water uptake of GDL is referred by the liquid water volume fraction in the sample and expressed by:

$$\varepsilon_l = \frac{W_{water} / \rho_w}{V_{GDL}} \quad (3-4)$$

where W_{water} is the weight of liquid water contained in the GDL, ρ_w is the density of water, and V_{GDL} is the geometric volume of the GDL. In order to measure the W_{water} , the GDL was first dried in oven at 105 °C for 4 hr to obtain its dry weight W_{dry} , and then the dried GDL was immersed in the boiling water for 2 hr to obtain the corresponding wet weight W_{wet} . The weight of water, W_{water} , is obtained from the difference of the wet and dry weights of the sample, $W_{wet} - W_{dry}$. This procedure was repeated until the constant weight of liquid water contained in the GDL was obtained. Before weighing, the sample was taken from water and surface water was removed using tissue paper. To reduce the testing errors, the testing procedure was repeated to

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obtain a constant water uptake (Fig.3-5). Five pieces of each type of sample were tested for this measurement. The mean value of the pieces of sample tested was used to plot figures. To assure that tested GDLs would present similar property, they were cut from the same sheet of GDL material.

Fig. 3- 5 The dependence of water uptake of CFGLD with varying PTFE content on the testing repeat times

3.3.6.2 Water uptake measurement of Nafion / Nafion-silica composite film

The water uptake of Nafion-silica composite was determined by the gravimetric analysis. The sample was prepared by spraying the Nafion-silica suspension onto one side of a glass plate with the dimension of 4 X 4 cm followed by drying in vacuum oven at 80 °C for 1 hr. The silica content in the samples varied with 0%, 3%, 6% and 10%. The Nafion loading on each sample was 1 mgcm⁻². The water uptake of Nafion-silica composite layer can be referred by the liquid water accumulation in the sample and expressed by:

$$\Phi_w = \frac{W_{water}}{W_{sample}} \quad (3-5)$$

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where, W_{water} is the weight of liquid water accumulated in each sample, and W_{sample} is the weight of the Nafion-silica composite layer from subtracting the weight of the coated glass plate with Nafion-silica from the glass plate. In order to measure the W_{water} , the sample was first dried in a vacuum oven at 105 °C for 4 hr to obtain the dry weight W_{dry} of sample using an electronic balance (Sartorius Basic balance, sensitivity of 0.1 mg), and then immersed in the hot water at 80 °C for 4 hr to obtain the wet weight W_{wet} of sample with the balance. The surface water was removed using a tissue paper prior to the W_{wet} measurement (this was carried out as quickly as possible to avoid weighing errors). The weight of water, W_{water} , is obtained from the difference of the wet and dry weights of sample, $W_{wet} - W_{dry}$. With each of analysed samples, five parallel analyses were performed.

3.3.7 Contact angle measurement

Contact angles are used as a measure of the wetting interaction between a liquid and a solid. The contact angle of a CFGDL was measured based on Wilhelmy method [Handbook of Fuel Cell, volume 3]. In this technique, a rectangular-shaped piece of diffusion media is dipped vertically into water and the weight of the diffusion media is measured with a balance. The value of the weight includes contributions from the wetting force (repelling or attracting force), $F_{wetting}$, caused by the water-to-solid interaction, and the buoyancy force, $F_{buoyancy}$. The contact angle can be calculated using the following equation:

$$F_{wetting} = L_{l,s} \cdot \sigma_l \cdot \cos \theta \quad (3-6)$$

where, $F_{wetting}$, the weight which is obtained from extrapolating of the plot of the weight value with the depth of GDL immersed into water to the zero depth; $L_{l,s}$ the length of the liquid-solid interface, i.e. the two times the sum of GDL width and

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thickness, i.e., $2 \times (\text{width} + \text{thickness})$; σ_l the surface tension (72 dyne/cm for water) and θ the contact angle.

A laboratory built-up device based on Wilhelmy technique is shown in Figure (3-6). In the measurement at 25 °C, the beaker filled with water is placed on the balance and tared. The sample is immersed into the water. The weight displayed on the balance is the wetting force and the buoyancy force. The change of the weight on the balance with the depth of immersion of the solid are recorded. The weight value as function of the depth of immersion is plotted as shown in Figure (3-7). The wetting force is obtained by extrapolating the graph back to zero depth of immersion to remove the effects of the buoyancy force and then the contact angle can be calculated using Eq.(3-6). With each of analyzed samples, five repeated analyses were performed.

Fig. 3- 6 The device for measurement of contact angle of carbon filled gas diffusion layer

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Fig. 3- 7 The Wilhelmy result with a carbon filled gas diffusion layer

CHAPTER 4 Investigation of Gas Diffusion Layer Structure for PEMFCs

CHAPTER 4 Investigation of gas diffusion layer structure for PEMFCs**4.1 Introduction**

In this chapter, a carbon-filled gas diffusion layer (CFGDL), which consists of electrical conductive carbon substrate with more macro-porous structure and conductive carbon/PTFE filler, was developed based on the GDL invented by Campbell *et al.* To understand fundamentally, the physical properties and electrochemical behaviors of the CFGDL, various physical techniques (SEM, EDX, FESEM, TEM, MIP) and electrochemical characterizations (CV, EIS, steady-state polarization) were carried out in comparison with the one-layer and dual-layer GDLs in this study. Many valuable results have been achieved as follows in the passage. Practical parameters obtained from this study could be useful for the fuel cell modeling research and the GDL design for PEMFC.

4.2 Experimental

TGP-H-030 carbon paper with specific area density of 4.2 mg cm^{-2} and thickness of 0.11 mm from Fuel Cell Store was chosen as one-layer GDL and used to make dual-layer GDL and CFGDL. The carbon paper contains about 20% PTFE after hydrophobic treatment. The procedure for the preparation of CFGDL is same as the method in Section 3.1.1 in Chapter 3. The carbon loading and PTFE content in the carbon/PTFE filler is 1.5 mgcm^{-2} and 40%, respectively, which is the optimal composition for CFGDL using TGP-H-030 carbon paper based on the study in Chapter 5. The micro-porous layer (MPL) with the carbon loading of 2 mgcm^{-2} and PTFE content of 35% was prepared for dual-layer GDL based on that reported by Qi and Kaufman [2002]. E-TEK 20 wt.% Pt/C catalyst was used to prepared the

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hydrophilic-type, i.e. thin-layer, catalyst layer and the Pt loading was 0.4 mgcm^{-2} . The Nafion112 was used to prepare the MEA for this study.

A single cell with ca. 1.5 cm^2 geometric electrode area and mesh flow field was used for all the steady-state polarization measurement, cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) measurements. This setup is considered to be suitable for the investigation of electrochemical behavior of GDL and electrode due to the reduction of flow field dimension effect. CV and EIS measurements were carried out after the steady-state polarization measurement using the same fuel cell setup.

4.3 Results and discussion

4.3.1 SEM and EDX analysis

The structure of the three different types of GDL was characterized by using scanning electron microscopy (SEM). Fig.4-1 shows scanning electron micro-graphs of cross-section of the three types of GDLs. The differences in the structure of the three types of GDLs are easily distinguished. The microstructure of one layer GDL (i.e. TGP-H-030 carbon paper) is characterized by a non-woven structure with many macro-open pores (Fig.4-1a). The thickness of the macro-porous sheet is about 0.11 mm. The orientation of the carbon fibers of TGP-H-030 is anisotropic in the in-plane and through-plane directions. The orientations of fibers are mostly parallel to the surface of the sheet. This indicates that the conductivity of the carbon paper may be anisotropic in the in-plane and through-plane directions. The non-woven fiber sheet was treated by immersion in PTFE emulsion to strengthen the structure and the surfaces become hydrophobic. The dual-layer structure of GDL made of a layer of macro-porous carbon fiber sheet (i.e., TGP-H-030 carbon paper, 0.11 mm in

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thickness) and a micro-porous layer (MPL) consisting of carbon/PTFE mixture (35 wt% PTFE and XC-72 carbon powder, carbon loading of 2 mg cm^{-2}) with a uniform thickness of 0.07 mm is illustrated in Fig.4-1b. A clear boundary between two layers and no intrusion of carbon/PTFE mixture into the macro-porous structure are observed. Fig.4-1c shows the carbon filled structure of GDL, *i.e.*, a layer of macro-porous carbon fiber sheet (TGP-H-030 carbon paper) filled with carbon/PTFE filler (40 wt% PTFE and XC-72 carbon powder, carbon loading of 1.5 mg cm^{-2}). The thickness of the structure was kept constant at the same value of 0.11 mm as the one of TGP-H-030 carbon paper. The carbon/PTFE conducting filler was uniformly disposed in the structure of the carbon paper. Thus, the conductivity of the carbon filled GDL would increase and be less anisotropic both in the in-plane and through-plane directions.

Fig. 4- 1 SEM micrographs of the cross-section images of the investigated GDLs (a) one-layer GDL, (b) dual-layer GDL and (c) CFGDL

Fig. 4- 2 SEM micrographs of the top-view images of the investigated GDLs (a) one-layer GDL, (b) dual-layer GDL and (c) CFGDL

Fig.4-2 shows the SEM micrographs of the top-view images of the three types of GDLs. TGP-H-030 carbon paper, which has a non-woven structure with many macro-open pores (Fig.4-2a), would have the poor support for Pt/C catalyst particles when

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the catalyst was directly deposited on its surface. The open structure of the carbon paper would cause the Pt/C catalyst particles and Nafion particle to drop inside the carbon paper, losing the active catalyst sites. The open space on the surface could also increase the contact resistance between the electrode and the membrane when using carbon paper as GDL. The GDL coated a thin layer of carbon and PTFE mixture, a dual-layer structure (Fig.4-2b), would improve the support for Pt/C catalyst particles when making the catalyst layer and the contact between the electrode and the membrane. The cracks on the coating surface may be caused by the fast evaporation of solvent in the carbon/PTFE paste. The carbon-filled GDL (Fig.4-2c) shows much smoother surface in comparison to the dual-layer GDL, and the numbers of cracks are much smaller. The much smooth coating surface produced is attributed to the wrapping of the carbon/PTFE mixture with the carbon fiber network structure in carbon paper. Thus, the carbon-filled GDL will have the same function as the dual-layer GDL for the support of Pt/C catalyst layer.

Fig.4-3 and Fig.4-4 show the EDX analyses for the catalyst layer surfaces and back faces (faced to the flow field plate) of the Nafion-treated electrodes with three types of GDLs. The EDX analyses on the catalyst layer surfaces of the three samples all show the presence of Pt, C, F and S, with more or less the same electron counts for each element (Fig.4-3). The chemical elements, Pt and C come from the Pt/C catalyst, and F and S from Nafion solution. However, the EDX analyses on the back faces of the same samples (Fig.4-4(a to c)) are different from that of the catalyst layer surface. The EDX analysis on the back face of the electrode using TGP-H-030 carbon paper as the backing shows the same chemical elements of Pt, C, F and S (Fig.4-4a) as the catalyst layer surface. It is obvious that the elements, Pt and S come from the Pt/C particles and Nafion polymer cross over the carbon paper, indicating that the macro-

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pore structure of one-layer GDL offers a poor physical support for the catalyst layer. This would result in some catalyst particles dropping into the structure of GDL, decreasing the utilization efficiency of Pt catalyst. The EDX analyses on the back faces of the electrodes with both the dual-layer and carbon-filled GDLs show the existence of C, F and S elements only and Pt was not detected, as seen in Fig.4-4(b and c). S is from Nafion polymer which crosses over the GDLs, indicating that the Nafion molecular penetrates easily through GDLs to the back face [X. Cheng et al, 1999]. The Nafion crossover to the back face of electrode may cause the some parts of GDL to be hydrophilic. In summary, the EDX analyses indicate that the Pt/C particles and Nafion polymer can easily penetrate through the one-layer structure GDL, i.e., TGP-H-030 carbon paper to the back face during the preparation of catalyst layer on the GDL. It strongly supports the evidence that the one-layer structure GDL has the poor support for Pt/C catalyst particles if the catalyst is directly deposited on its surface. The dual-layer and carbon-filled structure GDLs can effectively prevent the penetration of Pt/C particles through the GDL and largely reduce the crossover of Nafion polymer through the GDL as well.

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Fig. 4- 3 EDX analyses for the catalyst layer surfaces with the supports (a) one-layer, (b) dual-layer and (c) CFGDL

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Fig. 4- 4 EDX analyses for the back faces (faced to the flow field plate) of the electrodes with the supports (a) one-layer, (b) dual-layer and (c) CFGDL

4.3.2 Pore size distribution analysis

The porosity of GDL is a very important parameter for the design of gas diffusion electrode, since it significantly affect the reactants/product transport in the electrode. There is also a need to characterize this pore structure to provide the parameter of porosity for transport models. Fig.4-5 shows the cumulative pore volume (referred as to local porosity) and pore volume distribution in the gas diffusion layers (GDLs) with the three different types of structure obtained from mercury intrusion measurements. A summary of the porosimetric measurements is shown in Table 4-1.

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Table 4- 1 The pore characters of GDLs with varying structure

	Total porosity	Average pore diameter (μm)	Average pore diameter (μm)		local porosity	
			Primary pore	Secondary pore	Primary pore	Secondary pore
One-layer	0.77	35.8	4.3	40.3	0.095	0.675
Dual-layer	0.73	25.5	0.97	38.6	0.26	0.48
Carbon filled	0.67	4.7	2.3	30	0.61	0.06

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The cumulative pore volume significantly changes with varying the GDL structure, indicating the effect of the structure on the porous system of the GDL. The results in Fig.4-5 reveal the presence of a bimodal pore structure, identifying two different groups of pores in the all three types of GDLs in the present study. For one-layer structure of GDL, i.e. TGP-H-030 carbon paper, the first peak of pore volume distribution is located at a pore size of about 85 nm, that is comparable to the size of PTFE particles (100 nm), while the second peak with a broad distribution has an average pore size of 40.3 μm (Fig.4-5a). For the purpose of comparison, a boundary of 10 μm is chosen to separate the primary (<10 μm) and secondary (>10 μm) pores for the carbon paper. About 12 % of pore volume in one-layer structure of GDL is in the primary pore region and 88 % of pore volume resides in the secondary pore region (Table 4-1). It is believed that the formation of the primary pore is due to the small agglomerates of PTFE and binder on the non-woven carbon paper, while the secondary pore is produced by the random formation of carbon fibers, as seen in Fig.4-2a. For the dual-layer structure of GDL, i.e., TGP-H-030 carbon paper with a MPL, as seen in Fig.4-5b, the pore distribution shows the peak at a pore size of about 0.3 μm and 38.6 μm , respectively. This is similar to that of the one-layer structure of GDL. About 35% of pore volume in the dual-layer structure of GDL is located in the primary pore region, significantly higher than that of the one-layer GDL. It is apparent that the primary pores with an average pore size of 0.97 μm corresponds to a space within the carbon / PTFE agglomerates in the MPL and the secondary pores with an average pore size of 38.6 μm corresponds to a space from the open space of carbon paper matrix and coarse cracks on the surface of the MPL (Fig.4-2b). For the carbon-filled structure of GDL, i.e., TGP-H-030 carbon paper filled with carbon and PTFE mixture, the first peak of pore volume distribution with a very broad

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distribution ($0.47 - 2.7 \mu\text{m}$) has average pore size of about $2.3 \mu\text{m}$, while the second peak has an average pore size of about $30 \mu\text{m}$, as seen in Fig.4-5b. About 90% of pore volume located in the primary pore region and 10% in the secondary pore region (Table 4-1). It is believed that the first peaks of pore volume distribution correspond to a space within the carbon / PTFE agglomerates and the second peaks correspond to a space from the open space and coarse cracks on the surfaces, which is supported by the evidence of the SEM image in Fig.4-2c.

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Fig. 4- 5 The cumulative pore volume (referred as to local porosity) and pore volume distribution in the gas diffusion layers (GDLs) with (a) one-layer GDL, (b) dual-layer GDL and (c) CFGDL

4.3.3 Electrical resistances measurement

Fig.4-7 shows the experimental results of the electrical resistances of the three different types of GDL in the through-plane direction measured by the method described in Chapter 3 (Section 3.3.1). By linearly fitting the experimental data in Fig.4-7, the specific area resistances $R_{ASR,T}$ of the investigated GDLs can be obtained and listed in Table 4-2. It can be seen from Table 4-2 that the one-layer GDL presents a similar value of $R_{ASR,T}$ to CFGDL but a little smaller than CFGDL, while the dual-layer GDL has the highest R_{SAR} value among the investigated GDLs. The explanation is given in the following passage.

The electrical resistances of the three different types of GDL in the through-plane direction can be described by an equivalent electric circuit model, as seen in Fig.4-6. R_1 in the Fig.4-6 (a to c) represents the through-plane electrical resistance of macro-porous matrix, i.e., TGP-H-030 carbon paper. R_2 in the Fig 4-6b represents the electrical resistance of micro-porous layer (MPL), i.e., the thin layer of carbon/PTFE deposited on the carbon paper. R_3 in the Fig 4-6c represents the electrical resistance

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of carbon/PTFE filler embedded in the carbon paper. From the equivalent electric circuit models, one can derive that the carbon-filled GDL would present the smallest through-plane electrical resistance among the three different types of GDL, and the one-layer GDL would have a smaller resistance than that of the dual-layer GDL based on the equations embedded in Fig.4-6.

Fig. 4- 6 Equivalent electric circuit model of the three different types of GDL in the through-plane direction, (a) one-layer GDL; (b) dual-layer GDL and (c) carbon-filled GDL

Fig. 4- 7 I – V curve for the measurement of electrical properties of the investigated GDLs

Table 4- 2 The electrical properties of the investigated samples

Types of GDLs	One-layer	Dual-layer	CFGDL
Specific area resistance (mΩcm ²)	0.407	0.901	0.333

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4.3.4 Cyclic voltammogram characterization

Fig.4-8 shows the cyclic voltammograms (CVs) for the electrodes with different types of GDL structure measured in a single cell fixture with 1.5 cm^2 geometric area (GA) after the steady-state polarization measurement of fuel cells. The electrodes with different types of GDL structure have the same Pt loading of 0.4 mgcm^{-2} and Nafion loading of 1 mgcm^{-2} (dry weight). In the measurement, humidified argon (Ar) was passed through the working electrode compartment (cathode) and humidified hydrogen (H_2) through the counter electrode compartment (anode) under the operation at $55 / 50 / 25 \text{ }^\circ\text{C}$ ($T_{\text{Ar humidifier}} / T_{\text{cell}} / T_{\text{hydrogen humidifier}}$) and ambient pressure for both gases. As shown in Fig 4-8, there were similar hydrogen peaks for these three electrodes. The difference is only the peak height and area, which can be used to estimate the electrochemically surface area (ESA) of the electrodes with different types of GDL structure [Gasteiger et al., 2003]. Table 4-3 summarizes the electrochemically specific area (ESA) with the different three types of GDL extracted from the CV curves in Fig.4-8.

Table 4- 3 The ESA with the three types of GDL

Type of GDL	Columbic charges for H_2 desorption (mC cm^{-2})	ESA ($\text{m}^2 \text{ g}^{-1}$)
One layer GDL	47.4	56.4
Dual layer GDL	61.6	73.3
Carbon-filled GDL	61.9	73.7

From Table 4-3, it can be seen that the both dual-layer and carbon-filled GDLs have a similar electrochemically specific area (ESA) of platinum catalyst, which is much higher than that of one-layer GDL. The lower ESA of electrode with one-layer GDL corresponds to the crossover of catalyst to the opposite face through the one-layer

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GDL (Fig 4-4a). This again verified that one-layer GDL offers a poor physical support for catalyst layer, and the dual-layer GDL with a micro-porous layer and CFGDL with carbon-filled structure significantly improved the support properties of GDL for the catalyst layer.

Fig. 4- 8 the cyclic voltammograms (CVs) for the electrodes with different types of GDL structure

To calculate the Pt utilization of catalyst in an electrode, the size of the Pt particles in the catalyst Pt/C has to be measured. The most popular method for the examination of the particle size and distribution of the catalyst is the transmission electron microscope (TEM) [Cheng et al., 1999]. However, the TEM can not be applied to observe the particle size and distribution of catalyst on the practical electrode. In this study, the field emission scanning electron microscopy (FESEM) was used to directly observe the particle size and distribution of the catalyst on the electrode. Fig.4-9 shows the FESEM image and histogram of the Pt particle size distribution of E-TEK 20% Pt/C catalyst coated on the gas diffusion layer. The big particles in the FESEM images with the diameters in the 10 – 50 nm range are carbon, and the tiny bright points deposited on the big particles are Pt (since metal can reflect light in the observation). The Pt particles observed has a wide particle size distribution ranging

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from 2 to 10 nm and the average particle size is 3.15 ± 1.17 nm . It is in good agreement with the result from the TEM observation on the electrode as shown in Fig.4-10 [Blom et al., 2003]. Fig.4-11 shows the TEM image and histogram of the Pt particle size distribution of E-TEK 20% Pt / C catalyst. The big particles with a diameter of about 30 nm are carbon, and the tiny black particles are Pt. The Pt particles have a narrow particle size distribution ranging from 1.5 to 3 nm and the average particle size is 2.19 ± 0.45 nm , which is in agreement with the results reported elsewhere [Cheng et al., 1999]. The larger Pt particle size from FESEM measurement on the electrode as compared with that from the TEM observation of the Pt/C catalyst powder can be attributed to the thermal treatment of electrode during the preparation process. The thermal treatment of electrode could increase the Pt particle growth in Pt/C catalyst [Lee and Pyun, 2000].

The specific area (SA) of Pt catalyst can be calculated by the following equation:

$$SA = \frac{6 \times 1000}{21.4 \times d} (m^2 / g) \quad (4-1)$$

where, 21.4 is the density of platinum, and d is the average diameter of the Pt particles in the Pt / C catalyst (assuming the spherical shape of the Pt particles). Table 4-4 summarizes the particle size and surface area of Pt particles obtained from the FESEM and TEM images. The platinum utilization of catalyst with three different GDLs calculated based on the Pt surface area obtained from FESEM and TEM is listed in Table 4-5. The results presented in Table 4-5 indicate that the preparation of catalyst layer on the electrode could cause the loss of Pt surface area.

CHAPTER 4 Investigation of Gas Diffusion Layer Structure for PEMFC**Table 4- 4 Particle size and surface area obtained from FESEM and TEM images**

FESEM observation on the electrode		TEM observation on the catalyst powder	
Particle size (nm)	Specific area (m^2g^{-1})	Particle size (nm)	Specific area (m^2g^{-1})
3.15 ± 1.17	80	2.19 ± 0.45	128

Table 4- 5 The platinum utilization of catalyst with three different GDLs

Types of GDL	ESA (m^2g^{-1})	Pt utilization based on SA from FESEM	Pt utilization based on SA from TEM
One-layer GDL	56.4	70%	44%
Dual-layer GDL	73.3	91.6%	57.3%
CFGDL	73.7	92%	57.5%

Fig. 4- 9 (a) the FESEM image and (b) histogram of the Pt particle size distribution of E-TEK 20% Pt/C catalyst coated on the gas diffusion layer

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Fig. 4- 10 The TEM image of Pt particles and distribution in the piece of electrode [Blom et al, 2003]

(a)

(b)

Fig. 4- 11 (a) the TEM image of Pt particles and (b) histogram of the Pt particle size distribution of E-TEK 20% Pt / C catalyst

4.3.5 EIS analysis

The impedance spectra of a fuel cell with H_2 / air as reactants measured at voltages of 0.8 V and 0.55 V are presented in Fig.4-12 and Fig.4-13. At the cell voltage of 0.8 V, the size of semicircle for the reaction on the CFGDL, which primarily corresponds to the charge-transfer process, is the smallest. On the other hand, for the reaction on the

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one-layer GDL the polarization resistance is much larger. The electrode with CFGDL has higher electrochemical reaction activity than those with one-layer and dual-layer GDL. This is also consistent with the cyclic voltammograms results in Section 4.3.4. At the cell voltage of 0.55 V, the two impedance arcs are observed - the higher frequency arc is most likely due to the charge-transfer process, while the lower frequency arc is due to the diffusion, i.e., mass-transfer step. A large low frequency arc corresponds to higher diffusion resistance. In Fig 4-13, the dual-layer GDL showed the largest impedance arc and CFGDL produced the smallest impedance arc. The dual-layer GDL has a maximum diffusion resistance and this could be related to the micro-structure of GDL. Since the dual-layer GDL has a thick coating due to the introduced MPL over the backing and provide more micro-pores in its structure, the oxygen at cathode transport from the flow field to the catalyst layer become more difficult than one-layer GDL and CFGDL. Although the one-layer GDL has much higher gas permeability than CFGDL, the diffusion property is still not satisfactory due to the water flooding. In summary, the GDL structure has high impact on both charge-transfer and diffusion resistance processes. CFGDL provides the best electrochemical reaction performance and a good mass transport property.

Fig. 4- 12 The impedance spectra of a fuel cell with H₂ / air as reactants measured at voltages of 0.8 V

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Fig. 4- 13 The impedance spectra of a fuel cell with H_2 / air as reactants measured at voltages of 0.55 V

4.3.6 Fuel cell characterization

Fuel cell performance — The steady-state current-potential curves ($I - V$) of the PEMFC with the three different types of GDL structures are shown in Fig.4-14 and Fig.4-15 for fuel cells operating on oxygen and air oxidants, respectively. The measurements were carried out under 1.5 bar H_2 pressure and 1.5 bar pressure O_2 / air and the externally humidifying condition at 65/60/55 $^{\circ}C$ ($T_{\text{anode humidifier}} / T_{\text{cell}} / T_{\text{cathode humidifier}}$).

Fig.4-14 shows the polarization performance of fuel cells prepared with different GDL, using H_2 / O_2 as reactants. As seen from Fig.4-14, the initial drop of the polarization curve is due to an electrochemical activation process, which is controlled by the sluggish electrode kinetics of oxygen reduction at the cathode surface, and the following linear descent of the polarization curve with increasing current density is mainly due to ohmic overpotential (a large slope of the linear region represents a large internal resistance of a test fuel cell), which is attributed to the total internal resistance of the fuel cell. This includes the resistance (R_m) of the electrolyte membrane, the resistance (R_e) of the electrode materials [EG&G Services Parsons]

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and the contact resistance (R_c) between various fuel cell components. The departure of polarization curves from linear regions in the high current density region is due to the mass transport polarization. The curves in red color in the figures were fitted results according to the empirical equation proposed by Ticianelli et al. [1988]. The results show that the fits between the experimental and the predicted data were quite reasonable at the Tafel regime.

In the polarization curves in Fig.4-14, the largest slope of the linear region is observed with the one-layer GDL, the smallest slope with the CFGDL and the intermediate with the dual-layer GDL. It reveals that the fuel cell with the one-layer GDL presents the largest total internal resistance followed by with the dual-layer GDL. The CFGDL has the smallest internal resistance. In this case, the internal resistance is mainly related to the structure of GDL since the same preparation procedure of MEA, materials (membrane and catalyst) except GDL, and fuel cell fixture were used and tested under the same condition. It is believed that the poor support of the one-layer GDL, i.e., TGP-H-030 carbon paper, for the catalyst layer of electrode would cause a poor electrical contact between the catalyst particles and GDL and a poor ionic contact between the catalyst particles and Nafion membrane. This is indicated by the results of the SEM and EDX in Section 4.3.1. Although the introduction of a micro-porous layer (MPL) of carbon/PTFE between the carbon paper and catalyst layer can increase the electrical contact, the MPL of the dual-layer GDL also increased the electrical resistance of GDL as compared with the CFGDL.

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Fig. 4- 14 Performance curves of a fuel cell with three difference types of GDL using H_2 / O_2 as the reactants

The same can also be said of the effect of the GDL structure on the mass transport in the electrode. As can be seen in Fig.4-14, the cell potential in the high current density region is much higher for the reaction on the cell with the CFGDL than that with the one-layer GDL. For the H_2 / O_2 fuel cell, the significant voltage drop in the cell at high current densities is mainly attributed to water flooding [Kong et al., 2002], which is also related to the pore size distribution of GDL. For the one-layer GDL, 88 % of pore volume is in the secondary pore region (diameter from 10 to 100 μm). The macro-pores in the GDL will cause the Nafion polymer on the catalyst side permeating through the GDL structure to the opposite side when preparing the catalyst layer. The Nafion polymer permeated through the GDL would cause the GDL structure to be partly hydrophilic. At the low / intermediate current density, the water generated at the cathode is not enough to form an oxygen diffusion barrier in the GDL structure. In this case, the partial hydrophilicity of GDL may be helpful to remove the liquid water at the cathode. However, at the high current density, the water flux generated at the cathode will increase so that the water paths in GDL are unable to remove water efficiently. Thus, the water flooding of the GDL will occur

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forming an oxygen diffusion barrier. Under a saturation condition a water droplet will form at the interface and the size of the water droplet is proportional to the diameter of pore [Wilson et al., 1995]. Thus, larger water droplets would be formed within the macro-pores of the GDL at cathode to inhibit the oxygen diffusion. Wilson et al. suggested that micro-porous GDL were needed on the cathode side if the cell was to be operated under optimum well-humidified condition. Nam and Kaviani [2003] has verified the large water droplet formed at the interface of macro-porous GDL by environmental scanning electron micrographs (ESEM). This is the reason that the earliest departure from the linear drop in the cell potential vs. current density in the high current density region for the reaction with the one-layer GDL. For the dual-layer structure GDL, the addition of MPL would greatly reduce the Nafion polymer permeating through the GDL from the catalyst side to the opposite side so that the hydrophobicity of the carbon paper may not change. The water accumulation in the GDL is reduced too. In addition, the larger water droplet may not be extended to the interface of catalyst layer/MPL to flood the catalyst layer. However, larger water droplets would still be formed within the macro-pores of the carbon paper in the dual-layer GDL at the cathode side, inhibiting the oxygen diffusion. This appears to explain a better mass transport of the dual-layer GDL at the high current density than the one-layer GDL. For the CFGDL, the carbon/PTFE filler embedded in the carbon paper will play the same role as the dual-layer GDL to reduce the Nafion polymer permeation into the GDL. Meanwhile, the carbon/PTFE filler filled in the carbon paper also changes the pore size distribution in the GDL (the majority of pore volume is in the primary pores with pore size about 2 μm in diameter). In this case, only micro-water droplets will be formed in the GDL. The transport of the dispersed micro-water droplets through GDL will be relatively fast, decreasing the mass

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diffusion resistance for the oxygen. On the other hand, the hydrophobic carbon/PTFE filler may reduce the condensation rate of water vapor [Litster & Djilali, 2005] in the GDL. This explains the reason of no mass limitation observed in the cell with CFGDL in the current density range studied within project.

Fig. 4- 15 Performance curves of a fuel cell with three difference types of GDL using H_2 / air as the reactants

Fig 4-15 shows the typical pattern of the fuel cell polarization curves with varied the GDL structure when operating the cell with H_2 / air. The polarization curves were characterized by three polarization sources: (1) activation polarization (act), (2) ohmic polarization (ohm), and (3) concentration polarization (conc), similar to that operated with H_2 / O_2 . Similar to that in fuel cell operation, the activation polarization loss is dominant at low current density due to the sluggish electrode kinetics of oxygen reduction at the cathode. The ohmic polarization (loss) varies linearly with the current density. Different to that in the H_2 / O_2 fuel cell operation, the deviation from the linear region occurs at much lower current density most likely due to the lower partial pressure of oxygen. The concentration polarization losses become prominent at the high current density. It can be seen that the effect of the GDL structure on the polarizations in the activation and ohmic controlled regions in Fig.4-

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15 is similar to that under H_2 / O_2 operation (see Fig.4-14). However, a strong effect of the GDL structure on the polarization in the transport limitation controlled region is observed. For instance, the dual-layer GDL presents the lowest limiting current density of 1291 mAcm^{-2} ; CFGDL has the highest limiting current density of 1587 mAcm^{-2} and the one-layer GDL gives the intermediate limiting current density of 1374 mAcm^{-2} . CFGDL has the best oxygen transport property. The limiting current (i_L), which is representative of the oxygen transport limitation on the cathode of a fuel cell, is an important parameter that defines the quality of an electrode [Kocha, 2003]. It is further verified that the mass transfer property of GDL is largely related to their pore size distribution and structure.

One of the properties of a porous medium is the permeability, which is a measure of resistance due to convective flow. The permeability of GDL (porous medium) can be estimated by the following equation [Litster & Djilali, 2005]:

$$k = \frac{d_{\text{pore}}^2 \varepsilon^3}{36k_k (1 - \varepsilon)^2} \quad (4-2)$$

where d_{pore} is the pore diameter, ε is the porosity and k_k is Kozeny constant, which is about 5. Thus, the permeability of the GDLs can be obtained based on the data of average pore size and porosity in Table 4-1 and listed in Table 4-6 (for the dual-layer GDL, the MPL being dominant in the permeability is assumed).

Table 4- 6 the estimated permeability of three types of GDLs according to Eq.4-2

Type of GDL	One-layer (backing)	Dual-layer		CFGDL
		Total	MPL	
Permeability ($\times 10^{12} \text{ M}^2$)	61	19	0.31	0.34

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It is shown in Table 4-6 that the one-layer GDL, i.e., TGP-H-030 carbon paper, has two order magnitudes of the permeability greater than those of MPL in the dual-layer GDL and CFGDL. This indicates the MPL in the dual-layer GDL and carbon/PTFE filler in CFGDL contribute major fluid flow resistance to GDLs. The CFGDL has the same order of magnitude of the permeability as the MPL in the dual-layer GDL. A slightly higher permeability of CFGDL as compared to that of the MPL in the dual-layer GDL is probably due to the optimal composition of carbon/PTFE filler (1.5 mg cm⁻² of carbon and 40% of PTFE) embedded into the macro-porous substrate (0.11 mm and 4.2 mgcm⁻² of specific density). Such structure may have higher strength to resist the compressing and deformation during hot-pressing process, as compared to the dual-layer GDL. The higher permeability of CFGDL also corresponds to a larger limiting current compared with the dual-layer GDL. On the other hand, the significantly high permeability of the one-layer GDL only exhibited slightly higher limiting current than that of the dual-layer GDL, but lower than that of CFGDL. It indicates that the water flooding in the GDL at the high current density would play a dominant role on the limiting current region as discussed using H₂/O₂ as reactants.

In summary, CFGDL presents the best fuel cell performances and the one-layer GDL provides the worst fuel cell performance in the activation polarization / ohmic polarization controlled regions when using both H₂/O₂ and H₂/air as the reactants. In the mass transport limitation controlled region, the CFGDL shows the largest limiting current and the one-layer GDL provides a larger limiting current than the dual-layer GDL. In addition, it is clearly seen in Fig.4-14 and Fig.4-15 (power density vs. current density curves) that CFGDL also shows the highest maximum power density in comparison with both one-layer and dual-layer GDLs when operating with H₂/O₂ or H₂/air as the reactants.

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ORR kinetics analysis — Kinetic parameters, such as the Tafel slope, exchange current density and cell internal resistance can be obtained from H₂ / O₂ performance region where mass-transfer losses are negligible. The analysis of the polarization curves in this study is based on the following assumptions: negligible anode polarization; first order cathode reaction kinetics; insignificant hydrogen crossover, no internal short circuit of the cell and free of mass-transfer losses. The total cell resistance under H₂ / O₂ operating condition can be estimated by fitting the performance curve in the Tafel regime (over 0.8 V of cell potential where partial coverage of oxide species existed, the Tafel slope should be 60 mVdec⁻¹ and the reaction orders are 1 [Gattrell & MacDougall, 2003] with the semi-empirical equation [Ticianelli]:

$$E = E_0 - b \log i - iR_t \quad (4-3)$$

where $R_t = R_m + R_e + R_c$, which is constant at the sufficient humidification in the cell; b is Tafel slope and E_0 is the potential at 1 mAcm⁻² (iR_t is negligible at 1 mAcm⁻²). By fitting Eq. (4-3) to the experimental data in Fig.4-14, the kinetics parameters of three types of GDLs are obtained and listed in Table 4-7. Using the fitting results of the cell total resistances in Table 4-7 and the electrochemically specific active areas (ESA) from CV measurement in Table 4-3, the iR free (cell voltage corrected for resistance) linearized performance curve associated with the current density normalized to ESA is illustrated in Fig.4-16. The thermodynamic open circuit (E_{rev}) potential at 60 °C and under P_{O2}/ P_{H2}= 1.5 bar used in Fig.4-16 was estimated using the equation [Bernardi and Verbrugge, 1992] below to be 1.2 V:

$$E_{rev} = 1.23 - 0.9 \times 10^{-3} (T - 298) + 2.303 \frac{RT}{4F} \log(p_{H_2}^2 p_{O_2}) \quad (4-4)$$

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where R is the ideal gas constant, T the temperature in Kelvin, and F the Faraday constant. Thus, the exchange current density i_0 for ORR can be obtained by linearly extrapolating the experimental data to the thermodynamic potential E_{rev} to be in the range $10^{-8} - 10^{-9}$, which is in good agreement with the report by Kocha [2003]. The Tafel slope is the slope of the extrapolating line. Table 4-7 shows the kinetics parameters from the fitting the experimental data in Fig.4-14, exchange current density i_0 and the Tafel slope after the cell voltage corrected for resistance associated with the current density normalized to ESA.

Table 4- 7 ORR kinetics parameters

Types of GDL	E_0 (V)	b (i-V fitting/iR-free with i_{ESA}) (mV dec ⁻¹)	R_t (Ωcm^2)	i_0 ($\times 10^9 \text{ Acm}_{ESA}^{-2}$)
One-layer	0.993	59 / 60	0.25	1.61
Dual-layer	1.019	62 / 60	0.18	3.34
CFGDL	1.036	61 / 60	0.15	5.48

From Table 4-7, the structure of GDL significantly affects the kinetics parameters of E_0 , i_0 and R_t . The CFGDL has the highest value of E_0 , corresponding to the highest ESA value. This indicates that value of E_0 is related to the electrochemical active area of electrode. Since the electrical resistances of the investigated GDLs (see Table 4-2) are three orders of magnitude lower than R_t , the substantial difference of R_t for the three types of GDL is most likely due to the different contact resistances of the GDL. It is believed that the one-layer GDL would have highest contact resistance for both electron and proton conductions as mentioned in Section 4.3.1 and 4.3.2. Similar values of Tafel slope b around 60 mVdec⁻¹ were obtained by fitting Eq.4-3 (Table 4-7). Tafel slope b for ORR is related to the charge transfer coefficient, α , by the following equation.

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$$b = \frac{2.303RT}{2\alpha F} \quad (4-5)$$

where α is known as the charge transfer coefficient. The value of α describes the proportion of the electrical energy applied that is harnessed in changing the rate of the electrochemical reaction. Typically, the value of α ranges from 0.1 to 0.5 for the cathode, which is related to catalyst materials [Larminie & Dicks, 2000]. In this case, the value of α was estimated to be 0.5. The i_0 values in Table 4-7 fall in the range $10^{-8} - 10^{-9} \text{ Acm}_{\text{ESA}}^{-2}$ are reasonable and consisted with those reported by Kocha [2003].

Fig. 4- 16 The iR free (cell voltage corrected for resistance) linearized performance curve associated with the current density normalized to ESA

For a H_2 / air fuel cell, the polarization curve also includes the mass transport losses, and the gas transport losses under H_2 / air operation occur over the entire range of current density. In order to evaluate the effect of mass transport losses, we simulated a ideal polarization curve under H_2 / air operation based on the kinetics parameters of b and R_i from the fitting results for the H_2 / O_2 fuel cell. E_0 (considering the effect of O_2 partial pressure) was obtained from the polarization curves, using Eq.4-3 as shown

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in Fig.4-17. The difference between the ideal polarization curve (without mass transport losses) and experimental polarization curve was compared. Parameters b and R_t are considered to be constant for the cells studied. The results of ideal polarization curve under H_2 / air operation in comparison to the experimental curve are presented in Fig 4-18. The experimental data after corrected by the ideal polarization results (Fig 4-18d) shows the mass transport losses in the cells. Here, we propose a model equation based on the equation reported in the literature [EG&G Technical Services, 2005] for representing the mass transport loss referred as to concentration overpotential as follows:

$$\eta_{conc} = iR_{diff} + B \log \left(1 - \frac{i}{i_L} \right) \quad (4-6)$$

where, R_{diff} is the linear mass diffusion resistance, B is the constant which may not equal the Tafel slope b in Eq.4-3, i_L is the limiting current. Using the proposed model equation to fit the mass transport loss curve in Fig. 4-18d, the parameters R_{diff} , B , and i_L were obtained and are given in Table 4-8. From the Table 4-8, it can be seen that CFGDL gives the lowest linear diffusion resistance but the largest limiting current and the dual-layer GDL presents the highest linear diffusion resistance and smallest limiting current. It indicates that CFGDL has a better mass transport property than one-layer and dual-layer GDLs. It is consistent with the results of EIS measurement in Section 4.3.5. The constant B for the investigated GDLs has about three – four times higher than Tafel slope b .

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Table 4- 8 Kinetics parameters in the mass transport limitation controlled region

Type of GDL	Linear diffusion resistance, R_{diff} (Ωm^2)	Constant B ($Vdec^{-1}$)	Limiting current, i_L ($mAcm^{-2}$)
One-layer	0.06	0.218	1385
Dual-layer	0.08	0.279	1300
CFGDL	0.03	0.244	1593

Combined the model Eq.4-6 and the empirical Eq.4-3, a modified equation for representing the entire polarization curve under H_2 and air operation is given:

$$E = E_0 - b \log i - iR_t + iR_{diff} + B \log \left(1 - \frac{i}{i_L} \right) \quad (4-7)$$

Using Eq.4-7 with the parameters of b and R_t in Table 4-7 to fit the experimental polarization curves of H_2 / air fuel cell over the entire investigated current density range, the fitting results in the red lines in Fig.4-19 show that the fits between the experimental and the predicted data were quite reasonable.

Fig. 4- 17 H_2 / air fuel cell performance curves for extracting E_0 values

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Fig. 4- 18 the ideal polarization curves under H_2 / air operation without mass transport limitation compared with the experimental curves (a) one-layer GDL, (b) dual-layer GDL, (c) CFGDL and (d) the mass transport overpotentials for three types of GDL

Fig. 4- 19 H_2 / air cell experimental polarization curves fitted by using the proposed model equation (Eq.4-7) over the entire current density region

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5.1 Introduction

In the last chapter, a novel gas diffusion layer – carbon-filled gas diffusion layer (CFGDL) was developed and systemically investigated against the conventional one-layer and dual-layer GDLs. It was found that CFGDL offers the common advantages of both one-layer and dual-layer and overcomes their disadvantages. For instance, the embedded carbon/PTFE filler in the macro-substrate for CFGDL does not increase the thickness of GDL (optimal composition of carbon/PTFE) from the SEM observation in the cross-section; indicating that the diffusion distance for gas transport from the flow field to catalyst layer has remained constant. The carbon/PTFE filler in the structure also improved the microstructure of GDL as observed from the porosity characterization. A correct composition of carbon/PTFE filler would change the pore size distribution from the macro-scale (several ten micrometer) to sub-microscale (several micrometer), but almost remains in the ordinary diffusion controlled region for oxygen transport. In addition, the catalyst utilization was also increased due to the physical microstructure support for catalyst particles. The water management in the cell system was improved as well.

The objective in this chapter is to optimize the composition of a carbon-filled gas diffusion layer (CFGDL), to determine a structure and to understand the relationship between the surface morphology and microstructure of the CFGDL associated with the fuel cell performance [Han et al., 2006].

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5.2 Experimental

PE-704 carbon paper (SGL, SIGRATHERM[®] paper) with the specific area density of 4.1 g cm^{-2} , 0.3 mm in thickness and basically a macro-porous structure, was chosen as the electrode backing. Vulcan XC-72R carbon powder (Cabot Co.) was used as the electrically conductive filler and PTFE (60 wt. %, Aldrich) was used as the binder. E-TEK 20 wt.% Pt/C catalysts were used to prepare the hydrophobic-type catalyst layer where the Pt loading is 0.4 mg cm^{-2} . The Nafion112 was used to prepare the MEA for all of investigated samples. The preparation procedure for making CFGDL, electrode with CFGDL and MEA is reported in Section 3.1 of Chapter 3. To study the effect of carbon content in the CFGDL on the electrode performance, a set of CFGDLs with a fixed PTFE content (40%) was prepared by varying the carbon loadings from 2 to 8 mg cm^{-2} . Another set of CFGDLs with different PTFE contents (10 – 60%) and a fixed carbon loading of 6 mg cm^{-2} was prepared in the same manner.

A single cell with electrode area of 5-cm^2 and mesh flow field was used in the evaluation of the electrode performance. Steady state polarization and cyclic voltammetry (CV) were conducted on each sample. To investigate the effects of CFGDLs on the fuel cell polarization behaviors in the three polarization controlled regions (activation, ohmic and mass transport limitation polarizations), pure hydrogen and air were used as the reactants in the study. In the polarization measurements, the single cell was operated at 80°C and 1.5 bars on both anode and cathode using humidified H_2/Air as reactants. The anode gas humidification was set at 5°C higher than the cell temperature, while cathode air humidification was set at 5°C lower than the cell temperature. For reactant flows arranged in co-flow manner, the gas flow rates were kept at different stoichiometric values (1.15 times for H_2 and 2.5 times for air at 1 A cm^{-2} current density). The testing was carried out using Arbin electronic

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load system. In the CV measurements, the cell was operated at 70 °C under ambient pressure. Humidified argon (Ar) was fed to the working electrode compartment (cathode), while humidified hydrogen (H₂) was fed to the counter electrode compartment (anode). Because of the negligible over-potential at the counter electrode for H₂ oxidation, the counter electrode serves as the reference electrode. The sweep rate in the measurements was 50 mV s⁻¹ with a potential range of 0.0 ~ 1.5 V. The CV measurements were performed using Princeton Applied Research Potentiostat / galvanostat (Model/263A).

5.3 Results and discussion

5.3.1 Resistance of the CFGDL

Fig.5-1 shows the V-I curves of the CFGDL fabricated using different carbon contents with a fixed 40% PTFE and different PTFE contents with a fixed 6 mg cm⁻² carbon. The curves appear to be in straight lines, indicating that pure ohmic nature of V-I curves with little polarization contribution from the CFGDL and current collector interface. Thus the slope of the curves would be the area resistance of the CFGDL. The V-I curves indicate that both carbon and PTFE contents have significant effect on the resistivity of the carbon-filled gas diffusion layer.

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(a)

(b)

Fig. 5- 1 V-I curves of the CFGDL made (a) with different carbon contents and a fixed 40% PTFE and (b) with different PTFE contents and a fixed 6 mg cm⁻² carbon. The curves were measured in a single cell fixture at 25 °C [Bever et al., 1996; Han et al., 2006]

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(a)

(b)

Fig. 5- 2 Dependence of the resistivity, ρ , of the CFGDL on (a) the carbon content in the case of a fixed 40% PTFE and the line in the figure was fitted result and (b) the PTFE content in the case of a fixed 6 mg cm^{-2} carbon loading

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Fig.5-2 shows the dependence of the resistivity (ρ) of the CFGDL on the carbon and PTFE loadings. The resistivity of PTFE treated carbon paper was 3.1 Ωcm . With the addition of carbon filler, the resistivity of the CFGDL drops sharply with the increase of carbon loading from 0 to 2 mg cm^{-2} and then decreases almost linearly with the carbon loading until the carbon content reached $\sim 6 \text{ mg cm}^{-2}$ (Fig.5-2a). Further increase in the carbon content has little effect on the resistivity of the CFGDL. As the same single cell fixture was used for all the CFGDL measurements, the difference in the measured resistivity must be related to the carbon content in the CFGDL. This clearly shows that the carbon fillers in the CFGDL play an important role in the electrical conductivity of the CFGDL. In fact, the electrical system of CFGDL can be assumed to include two conducting networks, i.e., the macro-porous substrate (carbon paper) and the conductive filler (carbon and PTFE mixture). The network chains act as parallel conductors through the CFGDL [Bueche, 1972]. Hence,

$$\frac{1}{\rho} = \frac{V_m}{\rho_m} + \frac{V_f}{\rho_f}, \quad (5-1)$$

where subscripts m and f refer to macro-porous substrate and conducting filler, respectively. The V_m and V_f are the respective volume fractions of the macro-porous substrate and conducting filler. ρ_m and ρ_f are the resistivities of the macro-porous substrate and conducting filler, respectively. Note that the volume fraction of conducting filler V_f can be expressed as:

$$V_f = \frac{m_f}{d_f l}, \quad (5-2)$$

where m_f (g cm^{-2}) and d_f (g cm^{-3}) are the loading and density of the conducting filler in the macro-porous substrate, respectively, and l (cm) is the thickness of the macro-

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porous substrate. The loading of the conducting filler m_f can be given by the sum of the loading of conductive particle (carbon powder) m_c and the loading of polymer binder (PTFE) m_p ,

$$m_f = m_c + m_p = \left(\frac{1+\xi}{\xi}\right)m_c, \quad (5-3)$$

where ξ is the loading ratio of conducting particle to polymer binder. Rewriting the Eq. (5-1), the resistivity of CFGDL becomes

$$\frac{1}{\rho} = \frac{V_m}{\rho_m} + km_c, \quad (5-4)$$

where

$$k = \left(\frac{\xi+1}{\xi}\right) \cdot \frac{1}{\rho_f d_f l}. \quad (5-5)$$

If the loading ratio of conducting particle to polymer binder ξ is constant, then ρ_f and d_f will be fixed. For a given system, the thickness of macro-porous substrate l is known, and thus k becomes a constant. Hence, ρ as a function of m_c can be established using Eq.5-4.

The result of the fitting the experimental data ρ vs. m_c to Eq.5-4 was presented in Fig.5-2a. Good agreement between the experimental data points and predicted ρ vs. m_c relation from the curve fitting indicates that Eq.5-4 describing the relation of the resistivity to carbon powder loading for CFGDL in this experiment is valid. The assumption of two parallel conducting networks of electrical system in CFGDL structure is reasonable.

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The same can also be said for the effect of the PTFE content in the CFGDL on the resistivity of the gas diffusion layer. As mentioned above, CFGDL can be considered to be two parallel conducting networks, macro-porous substrate (carbon paper) and conductive filler (carbon and PTFE mixture). The resistivity of conductive filler is dependent on the loading ratio of carbon powder to PTFE. When carbon loading in the filler is fixed, the resistivity must be the function of PTFE content. Based on Percolation Theory [Fiske et al, 1997], the resistivity of carbon/polymer conductive filler does not increase linearly with increasing polymer content. Instead, the resistivity increases sharply over a narrow range of polymer content. This increase in resistivity is due to the formation of barriers to conductive paths by PTFE, which is an insulating material, at the critical PTFE content. Below the critical PTFE content the conductive filler in CFGDL has sufficient continuous conductive networks and shows a high electrical conductivity. Above the critical PTFE content, the conductive filler would exhibit a poorer conductivity. This critical PTFE content also refers to the percolation threshold value for the electrical property of CFGDL. In the cases of CFGDL with a carbon content of 6 mg cm^{-2} , the resistivity of the CFGDL is more or less the same for different PTFE content until it reached 40%. Above the PTFE content of 40%, the resistivity of the CFGDL increased abruptly with the PTFE (Fig.5-2b). It is evident that the PTFE content of 40% is the critical PTFE content (percolation threshold value) and the conductive filler network contributes more effect on the resistivity of CFGDL than macro-porous substrate (carbon paper) network in CFGDL.

Thus, from the conductivity measurements and theoretical analysis above, it can be found that the carbon content of 6 mg cm^{-2} and 40% PTFE is the optimum composition for CFGDL to achieve the best electrical property.

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5.3.2 Morphologies analysis from SEM observation

Fig.5-3 shows the SEM micrographs of the SGL704E carbon paper before and after the hydrophobic treatment (PTFE immersion). SGL704E carbon paper has a non-woven structure with many open and large pores (Fig.5-3a). After the hydrophobic treatment by immersion in PTFE emulsion, SGL704E becomes much stronger in the mechanical strength due to its fibers bonded by PTFE. In addition, the fiber surfaces of carbon papers have become hydrophobic, which is helpful for water management in the electrode. There are still a lot of open spaces and large pores in SGL704E carbon paper structure although the porosity is reduced slightly by the PTFE treatment as can be seen in Fig 5-3b.

Fig. 5- 3 SEM micrographs of the SGL704E carbon paper (a) before and (b) after the hydrophobic treatment (PTFE content: 40%)

Fig.5-4 shows the SEM micrographs of the top-view and cross-section view of the CFGDL with carbon loading of 2 mg cm^{-2} to 8 mg cm^{-2} . The microstructure of the CFGDL with carbon loading of 2 mg cm^{-2} was characterized by the formation of large number of coarse cracks on the surfaces and large pore (Figs.5-4a&b). The large cracks and open space and pores in the CFGDL would lead to poor electrical conductivity of the CFGDL as shown by the high area specific resistance (Fig.5-2a). The large crack could also increase the contact resistance between CFGDL and catalyst particles and reduce the support to the catalyst as Pt catalyst particles may

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have fallen into the open pores of the gas diffusion electrode. This explanation is supported by the relatively low Pt utilization for the CFGDL with low carbon content (Fig.5-8a). Increase in the carbon loading reduced the number of cracks and the size of cracks. From the cross-section images, the large pore and open space of the CFGDL were also significantly reduced with the increase in the carbon content. In the case of CFGDL with carbon loading of 6 mg cm^{-2} , the microstructure of the diffusion layer was characterized by micro-pores uniformly distributed across the whole layer (Figs.5-4e&f). Such microstructure appears to be beneficial not only to the electrical conductivity (Fig.5-2a) but also to the support of the Pt catalyst (high Pt utilization as shown in Fig.5-8a). The high cell performance observed on the CFGDL with carbon loading of 6 mg cm^{-2} can also be explained by the right microstructure combined with proper hydrophobicity. However, further increase of the carbon loading to 8 mg cm^{-2} led to the formation of dense microstructure, as shown in Fig.5-4h. The dense microstructure would increase the gas diffusion resistance and this explains its reduced cell performance and relatively low limiting current density as compared to the cell with CFGDL having carbon content of 6 mg cm^{-2} (Fig.5-9). The present results clearly demonstrated that there is a close relationship among the microstructure, electrical conductivity, gas diffusion and the cell performance.

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Fig. 5- 4 SEM micrographs of the top-view and cross-section images of the CFGDL with carbon loading of (a) and (b) 2 mg cm⁻², (c) and (d) 4 mg cm⁻², (e) and (f) 6 mg cm⁻², and (g) and (h) 8 mg cm⁻². The PTFE content of the CFGDL was 40%

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5.3.3 Microstructure analysis based on the pore size distribution

Fig.5-5 shows the pore size distribution in the gas diffusion layers (GDLs) with different carbon loading at a fixed PTFE content of 40% compared to the PTFE treated carbon paper with different PTFE content at a fixed carbon loading of 6 mgcm⁻² obtained from mercury intrusion measurements. A summary of the porosimetric measurements is shown in Table 5-1 and Table 5-2.

From Fig.5-5a, it can be seen that by the introduction of the carbon/PTFE filler into the PTFE treated carbon paper the pore size distribution was significantly changed. The PTFE treated carbon paper presents a single peak located at the pore diameter of about 40 μm , while the CFGDL displays a similar pore size distribution model - bimodal pore structure, in which a clear boundary of 10 μm can be seen. The CFGDLs with the various carbon loadings have a similar location of the peak with the pore diameter of less than 10 μm , but the CFGDL with the carbon loading of 8 mg cm⁻² presents a broader pore size distribution. For the CFGDL, the volume of pore with the diameter over 10 μm is largely reduced. It reveals that the open and large pores shown in Fig.5-3 were filled by the carbon/PTFE filler. The effect of PTFE on the pore size distribution is clearly seen in Fig.5-5b. The lower the PTFE content in the carbon/PTFE filler of CFGDL, the broader the peak in the range with the pore diameter less than 10 μm will be. To further analyze the effects of the carbon loading and PTFE content on the microstructure in the CFGDL, the pores in the CFGDL are divided into the following four size ranges, (a) pore diameters less than 0.1 μm (corresponding to the space built by carbon particles/PTFE fiber), (b) pore diameters between 0.1 and 1 μm (corresponding to the space built by carbon/PTFE agglomerates), (c) pore diameters between 1 μm and 20 μm (corresponding to the space built by the carbon/PTFE agglomerates associated with

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carbon fiber), and (d) pore diameters larger than 20 μm (corresponding to the coarse crack on the surface and large pores in Fig.5-4) as shown in Table 5-1 and 5-2. This partition of the porosity coincidentally matches the function of pores in each pore size range. In the knowledge from the reference [Litster & Djilali, 2005], the pore size range of less than 0.1 μm is the Kundsens diffusion control regime for O_2 transport, the range between 0.1 and 1 μm is the Kundsens transition regime and the range between 1 and 20 μm is mainly controlled by the ordinary diffusion, however, above the range of 20 μm the drop of catalyst particles and Nafion polymer would occur when making catalyst layer. Fig.5-6 illustrates the effects of carbon loading and PTFE content on the local porosity (defined as the ratio of volume of pores in a certain size range to the total volume of CFGDL) based on the data listed in Table 5-1 and 5-2. It is found that the total porosity of CFGDL is significantly decreased with increasing carbon loading under a fixed PTFE content and varying PTFE content but fixed carbon loading; and majority of pores in the CFGDL is located in the pore size range of 1 - 20 μm . In this pore range, the carbon loading in the CFGDL significantly affects the local porosity. The local porosity first increases with increasing carbon loadings from 0 to 4 mgcm^{-2} and then decreases from 4 to 8 mgcm^{-2} shown in Fig 5-6a. It is believed that the optimal carbon loading range is between 4 and 6 mgcm^{-2} taking into the consideration of the effect of large pore in the range above 20 μm . It can be seen the local porosity in the pore size ranges of 0.1 – 1 μm and > 20 μm is apparently decreased with increasing carbon loading but the optimal local porosity is presented in the pore size range of 1 - 20 μm where the porosity is increased with increasing carbon loadings from 2 mgcm^{-2} to 4 mgcm^{-2} and then decreased from 4 mgcm^{-2} . The same can be said for the effect of the PTFE content in the CFGDL on the local porosity in the pore size range of 1 - 20 μm . it is found that the CFGDL with

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the PTFE content of 40% presents a maximum local porosity in this pore size range, which falls in the ordinary diffusion controlled regime (Fig.5-6b). In summary, the carbon loading under a fixed PTFE content and varying PTFE content but fixed carbon loading significantly changes the microstructure of the CFGDL. The local porosity in the ordinary controlled regime (1 – 20 μm) is the main contribution to the total porosity of CFGDL. It is believed that the optimal composition of CFGDL should be the carbon loadings between 4 – 6 mgcm^{-2} and PTFE content of 40% based on the analysis of pore size distribution in the study.

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Fig. 5- 5 The pore size distribution in the gas diffusion layers (GDLs) with (a) varying carbon loading at a fixed PTFE content of 40% compared with the PTFE treated carbon paper and (b) varying PTFE content at a fixed carbon loading of 6 mgcm^{-2} obtained from mercury intrusion measurements

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Table 5- 1The effect of carbon loading on the porosity of investigated samples

Carbon content (mgcm ⁻²)	Total porosity, ε_t (%)	Average pore diameter, $d_{t,a}$ (μm)	Pore size distribution							
			< 0.1 μm		0.1 – 1 μm		1 – 20 μm		> 20 μm	
			ε_i (%)	$d_{i,a}$ (nm)	ε_i (%)	$d_{i,a}$ (μm)	ε_i (%)	$d_{i,a}$ (μm)	ε_i (%)	$d_{i,a}$ (μm)
0	90	53	3.1	70	2.3	0.276	7.29	10	77	61
2	82	10.9	1.3	45	18	0.66	50	2.9	12.7	58
4	75	8.45	1.2	44.8	16.5	0.66	53	3.1	8.6	54.4
6	66	6.1	1.1	45	14.4	0.66	44.9	3.0	5.6	47
8	60	4.9	5.9	66.5	14.9	0.5	34.7	3.3	4.6	38.2

Note: (1) ε_t is total porosity; (2) ε_i is the local porosity; (3) $d_{t,a}$ is the average pore diameter of total pores of sample; and (4) $d_{i,a}$ is the average pore diameter of the pores in the local region.

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Table 5- 2 The effect of PTFE content on the porosity of investigated samples

PTFE content (%)	Total porosity, ε_t (%)	Average pore diameter, $d_{t,a}$ (μm)	Pore size distribution							
			< 0.1 μm		0.1 – 1 μm		1 – 20 μm		> 20 μm	
			ε_i (%)	$d_{i,a}$ (nm)	ε_i (%)	$d_{i,a}$ (μm)	ε_i (%)	$d_{i,a}$ (μm)	ε_i (%)	$d_{i,a}$ (μm)
10	71	5	1.3	43.5	23.6	0.52	41.2	3.37	4.9	38.2
20	70	5.3	1.6	51	19.5	0.59	43.9	2.94	5.0	43.3
30	68	5.76	1.6	49	17	0.6	44.2	3.0	5.2	46.5
40	66	6.1	1.1	45	14.4	0.66	44.9	3.0	5.6	47
50	63	6.7	0.64	52	13.8	0.66	42.8	3.15	5.8	41.3
60	58	7.5	0.56	40	10.8	0.69	40.5	3.24	6.1	47.6

Note: (1) ε_t is total porosity; (2) ε_i is the local porosity; (3) $d_{t,a}$ is the average pore diameter of total pores of sample; and (4) $d_{i,a}$ is the average pore diameter of the pores in the local region.

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(a)

(b)

Fig. 5- 6 The effects of (a) carbon loading and (b) PTFE content on the local porosity based on the data listed in Table5-1 and 5-2

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5.3.4 Cycle voltammetry measurement

Fig.5-7 shows the cyclic voltammograms of the CFGDL with different carbon and PTFE contents measured at 70 °C under the scanning rate of 50 mV s⁻¹. The peak associated with the hydrogen desorption at 0.17 ~ 0.22 V is clearly affected by both the carbon and PTFE content in the CFGDL. In the case of the CFGDL with a fixed 40% PTFE, the peak height at 0.177 V (i.e., the hydrogen desorption peak) increased with the increase in the carbon content (Fig.5-7a), implying the electrochemically active area (*ESA*) of electrodes and Pt utilization (the ratio of the *ESA* to *SA*, the Pt particle surface area of catalyst) increased with the increase in the carbon content in the CFGDL. Similarly in the case of CFGDL with a fixed carbon content of 6 mg cm⁻², the height of the hydrogen desorption peak at 0.182 V increased with the increase in the PTFE content (Fig.5-7b). The *ESA* of electrodes and Pt utilization can be estimated from the cyclic voltammograms assuming that the value of 0.21 mC cm⁻² for the hydrogen desorption charge on the smooth Pt electrode [Capon and Parsons, 1973; Antolini et al., 1999] and Pt surface area of 140m²g⁻¹ for E-TEK 20 wt.% Pt/C catalyst [Cheng et al., 1999].

Fig.5-8 shows the Pt utilization of the CFGDL as a function of carbon and PTFE contents, estimated from the cyclic voltammetry curves. In the case of CFGDL with 40% PTFE content, the Pt utilization increases with the increase of carbon loading in the CFGDL (Fig.5-8a) from 15.7% (carbon loading: 2 mg cm⁻²) to 51.8% (carbon loading: 8 mg cm⁻²). It can be explained that, at low carbon loading, the macro-pore structure of electrode backing will be inadequately filled with carbon black filler, thus offering poor physical support for the catalyst layer. It is in agreement with the higher local porosity in the pore size above 20 μm with the carbon loading of 2 mgcm⁻² as shown in Fig.5-6a. This would probably result in, when preparing the catalyst layer,

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some catalyst particles may have dropped into the electrode backing. Thus, the catalyst layer may not attach well to the Nafion membrane causing poor ionic contact and reduced *ESA*. It is also observed that there is no significant effect of PTFE content in the carbon filler of CFGDL on the Pt utilization, except for the case with 60% of PTFE content (Fig.5-8b). This is likely due to covering of PTFE agglomerates on some reactive sites with excessive PTFE in the carbon filler. This implicitly means that with reasonable amount of carbon content, the PTFE content in CFGDL is unlikely the key factor affecting the Pt utilization in the catalyst layer.

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(a)

(b)

Fig. 5-7 Cyclic voltammograms of the CFGLD with (a) different carbon content and (b) different PTFE content. The voltammograms were measured at 70°C and scanning rate of 50 mV s⁻¹. The Pt loading of the cathode was 0.4 mg cm⁻²

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(a)

(b)

Fig. 5- 8 Pt utilizations of the cells with (a) different carbon and (b) different PTFE contents in the CFGDL of the cathodes, estimated from the cyclic voltammograms of Fig.5-7. The Pt loading of the cathode was 0.4 mg cm^{-2}

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5.3.5 Cell performance

The performances of fuel cells operating at 80 °C under H₂/air with different carbon loadings and PTFE contents in the CFGDL of cathodes are shown in Fig.5-9 and 5-10, respectively. The curves in the figures were fitted results according to the empirical equation proposed by Srinivasan et al. [1988]. Results shown that the fittings between the experimental and the predicted data were quite reasonable in the low to intermediate current densities.

Fig. 5- 9 Polarization curves of the cells with different carbon loadings in the CFGDL of cathodes operating at 80 °C under H₂/air. The PTFE content in the CFGDL was 40% and the lines in the figure were fitted results

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Fig. 5- 10 Polarization curves of the cells with different PTFE contents in the CFGDL of cathodes operating at 80 °C under H₂/air. The carbon content in the CFGDL was 6 mg cm⁻² and the lines in the figure were fitted results

5.5.3.1 Effect of carbon loading

Fig.5-9 reveals clearly that increasing the carbon loading in CFGDL has a significant improvement in performance up to 6 mg cm⁻² in all three polarization regions, i.e., activation (mainly at the cathode), mass transport, and ohmic controlled, but further increasing carbon loading has little effect on the performance in activation and ohmic controlled regions but noticeable deterioration in mass transport region. An analysis of the results above is presented as follows.

In the activation polarization region, the reduced current density with decreasing the carbon loading is due to the loss of a number of active sites for the oxygen reduction reaction (ORR) inside the catalyst layer. At lower carbon loading, insufficient conductive filler (carbon powder with PTFE) in the structure of macro-porous substrate (carbon paper) results in the catalyst particles dropping into the structure of CFGDL during the fabrication stage of catalyst layer. The catalyst particles dispersing into the structure of GDL become inactive for ORR. In other words, it in fact lowers

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the Pt loading in the electrode. It has been proven by the evidence of the increase in the ESA / Pt utilization of electrodes with the increase of the carbon loading (Fig.5-8a).

In the ohmic controlled polarization region, the cell overpotential is resulted from the internal resistances (i.e., the value of R_i produced by fitting of the empirical equation proposed by Srinivasan et al. to experimental data in Fig.5-9) of the cell including the resistances of the membrane and various electrode layers, mass transport resistance, and the contact resistances both between membrane and electrodes and between electrodes and polar plates. In this experiment, the main contribution to the internal resistance is from the low carbon loading in CFGDL when PTFE content is fixed at 40%, since the resistance of membrane, which is strongly dependent on the water content inside would not change assuming that the membrane is fully hydrated under the humidifying condition [Zawodzinski et al., 1993]. The decrease in the internal resistance or ohmic overpotential with increase of carbon loading up to 6 mgcm^{-2} in the ohmic controlled region is dependent on decrease in the area specific resistance ($R_{ASR,T}$) of CFGDL and contact resistance (between electrode and membrane). The decrease in $R_{ASR,T}$ of CFGDL with increasing carbon loading has been mentioned in Section 5.3.1. By comparison, $R_{ASR,T}$ of CFGDL is two orders of magnitude smaller than that of the R_t of the cell as seen in Fig.5-11a. The major contribution of carbon loading in CFGDL to the R_t is due to the electrical contact resistance between the CFGDL and the catalyst layer and ionic contact resistance between the electrode and the membrane [Paganin et al., 1996]. In other words, if there is insufficient carbon black filler in the macro-structure of the gas diffusion layer, it may not be able to give

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a good support for catalyst layer. This could give rise to increase in the internal resistance of the cell with increasing in the contact resistances.

(a)

(b)

Fig. 5- 11 Plots of the cell internal resistance, R_t , against the (a) carbon and (b) PTFE contents of the CFGDL. R_t was evaluated from the polarization curves of Fig.5-9 and 5-10. In comparison, the area specific resistance, $R_{\text{ASR},T}$ of the CFGDL measured in the single cell fixture was also given in the figure

The increase in carbon loading from 2 to 6 mg cm^{-2} in CFGDL also increases the mass transport limiting current densities in the mass transport control polarization

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region as seen in Fig.5-9. These results contradict those reported by Jordan et al. [2000] and Kong et al. [2002]. These contradictory results might be due to the different structure of CFGDL to GDL's in the conventional three-layer electrode. In the CFGDL, the conductive filler (carbon powder with PTFE) is filled into the whole structure of the macro-porous substrate (carbon paper) to form a homogeneous porous structure in the CFGDL, whose thickness remains unchanged under varying carbon loading. The CFGDL with low carbon loading has more big pores with pore size larger than $20\text{ }\mu\text{m}$ (Table5-1 and Fig.5-6a) in the carbon paper, and these big pores retain larger water droplets in the macro pores of CFGDL leading to the increased mass transport resistance for oxygen diffusion [Wilson et al.]. Thus, the electrode with lower carbon loading in CFGDL showed a larger mass transport over-potential. For the GDL used in the three-layer electrode, however, a micro-porous layer of carbon black with PTFE is coated on a macro-porous substrate (carbon paper or carbon cloth). The extra carbon layer on the macro-porous substrate will increase the thickness of the GDL in the electrode with increasing the carbon loading. The increase in GDL thickness would reduce the gas accessing to the catalyst layer and thus increase the mass transport over-potential. The similar behavior can be observed in the case of carbon loading with 8 mg cm^{-2} in CFGDL seen in Fig.5-9. This is likely due to excessive use of carbon filler, thus decreasing the porosity of CFGDL, which has been verified by the porosity measurement in Section 5.3. This would cause increase in gas diffusion resistance of the CFGDL, as indicated by the relatively low limiting current density of the CFGDL with carbon loading of 8 mg cm^{-2} as compared to that of 6 mg cm^{-2} (Fig.5-9).

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5.5.3.2 Effect of PTFE content

Fig.5-10 is the polarization curves of the cells with different PTFE loadings in the CFGDL of cathodes operating at 80 °C under H₂/air. The carbon content in the CFGDL was 6 mg cm⁻² and the curves in the figure are the fitted results. Unlike the effect of carbon loading, the PTFE content of the CFGDL affects the polarization performance of the cell only in the ohmic and mass transport control polarization regions. Less impact of PTFE content on the performance in activation control region is observed. The best results were obtained on the cell with CFGDL having PTFE contents of 30-40%. Low PTFE content of 10% or high PTFE content of 60% will lead to reduced cell performance.

As mentioned earlier, the variation of PTFE content in CFGDL with carbon loading of 6.0 mg cm⁻² has less effect on the *ESA* / Pt utilization of electrode (Fig.5-8b) due to insignificant loss of catalyst particles from catalyst layer. This might be the reason that the PTFE content has less effect on the performance of the cell in the activation controlled polarization region.

The effect of PTFE content in the CFGDL with fixed carbon loading of 6 mg cm⁻² on the cell internal resistances (the value of R_i is produced by fitting of the empirical equation proposed by Srinivasan et al. to experimental data in Fig.5-10) in ohmic controlled polarization region as can be seen in Fig.5-11b. R_i does not change significantly with the PTFE content for the CFGDL with PTFE content lower than 40%. This is also in consistent with the dependence of the area specific resistance (R_{ASR}) of the CFGDL on the PTFE contents as shown in Fig.5-2b. With the PTFE content higher than 40%, the total cell resistance begins to increase, which is also in consistent with that of the area specific resistance of the CFGDL. In comparison, R_{ASR}

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of CFGDL is still two orders of magnitude smaller than that of the R_t of the cell with varying PTFE content in CFGDL (Fig.5-11b). It is believed that the major contribution of PTFE content in CFGDL to the R_t is from the electrical contact resistance between the CFGDL and the catalyst layer and the resistance associated with mass transport limitation. Below the PTFE content of 40%, the electrical contact resistance would play a significant role in the R_t . Above PTFE of 40%, both the electrical contact resistance and the resistance of mass transport would contribute equally important to R_t .

Mass transport losses in GDL come from the resistance of gas diffusion and the transport loss due to water flooding in an operating fuel cell. The gas diffusion rate in GDL is related to the porosity and thickness of GDL. The high porosity and thin GDL are helpful for reactants to access to the catalyst sites through the GDL. Introducing the hydrophobic agent, PTFE, inside the GDL structure, can alleviate the water flooding of GDL. This is because water may not be able to form stable droplets inside of hydrophobic micro-pores in the GDL; hence the GDL is less likely to be flooded. This implies that the catalyst layer that is in direct contact with the GDL will also be less likely to be flooded [Qi and Kaufman, 2002]. However, the hydrophobic property of GDL is dependent on the PTFE content in the GDL. The higher the content of PTFE contained in the GDL, the more hydrophobic the surface and micro-pores in GDL will be, and the less the electrode will be flooded. Thus, the mass transport losses due to water flooding will decrease. On the other hand, the increase of PTFE content in GDL also decreases the porosity/gas permeation of GDL [Lim and Wang, 2004]; it is consistent with the results shown in the Section 5.3. In the case of the CFGDL with an optimum carbon loading of 6 mg cm^{-2} , the primary function of the PTFE contents in the CFGDL is to improve the hydrophobic properties of the porous

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structure of the gas diffusion layer, which is critical to the gas diffusion and water removal through the GDL. It is evident that the polarization curve of fuel cell with PTFE content of 10%, exhibits the smallest mass transport limiting current density due to serious degree of flooding problem in CFGDL, and the mass transport limiting current density increases to the maximum value when the PTFE content reaches 30%, and then decreases with further increasing PTFE content due to decreasing the porosity of CFGDL at higher PTFE content (Fig5-10).

CHAPTER 6 Effect of PTFE content on the mass transport in the gas diffusion layer for PEMFCs

6.1. Introduction

The water management property of gas diffusion layer (GDL) in the electrode has a significantly effect on the performance of the polymer electrolyte fuel cell (PEMFC). The introduction of hydrophobic polymer (such as PTFE) into the structure of GDL could improve the water management in the GDL. The effect of PTFE on the performance and properties of GDL have been reported in a number of papers [Giorgi et al., 1998; Lim and Wang, 2004; Lin and Nguyen, 2005; Ioroi et al., 2003; Park et al., 2004; Qi and Kaufman, 2002; Jordan et al., 2000]. All these studies were focused on the optimization of PTFE content in a single-layer (a macro-porous carbon paper as GDL) or dual-layer (a carbon paper with a micro-porous carbon/PTFE sub-layer) structures of GDLs, and the effect of PTFE on porosity/pore size distribution and hydrophobicity of the GDL for understanding the mass transport of reactant gases/liquid product through the GDL. However, there are only handful of reports on the quantitative investigation of the basic parameters such as the water saturation, the liquid volume fraction and gas volume fraction of the gas diffusion layer (GDL) for two-phase flow and transport in the GDL, and the effect of these parameters on the performance of PEMFC.

The mass transport rate for both gases and water through GDL is significantly dependent on the pore system of GDL (its most important characteristics are porosity and pore size distribution). The effective gas diffusion coefficient in the porous media is a function of porosity which obeys the power law according to the Bruggemann equation [Bird et al., 2001]. Bevers et al. [1996] suggested that the pore size

distribution might affect the water management in the diffusion layer in relation to the water condensation phenomena which predicted that water condensation will first occur in small hydrophilic pores beyond actual saturation pressure. The small pores filled with water no longer contribute to gas transport. Kong et al. [2002] summarized that pore size distribution is a more important structural parameter in affecting the cell performance than the total porosity. It is believed that larger pores in the diffusion layer would prevent electrodes from water flooding based on the study. The pore system changes with the change of hydrophobic polymer loading. In theory, the porosity of carbon paper decreases with the increase in mass fraction of hydrophobic polymer after the hydrophobic treatment according to the following equation [Lim and Wang]:

$$\varepsilon = \varepsilon_0 - \frac{x_{HP}}{1 - x_{HP}} \cdot \frac{\rho_{CP}}{\rho_{HP}} \quad (6-1)$$

where, ε_0 is the porosity of carbon paper before hydrophobic treatment, x_{HP} the mass fraction of hydrophobic polymer, ρ_{CP} and ρ_{HP} the bulk density of carbon paper and the density of hydrophobic polymer, respectively. The decrease of pore volume in the carbon paper with increasing PTFE content was also reported by Mathias et al. [2003]. Hence, investigation of the effect of PTFE content in the carbon-filled gas diffusion layer (CFGDL) on the porous property and wetting property is necessary. The objective of this work is to gain more fundamental insights on the total porosity, local porosity and pore size distribution associated with liquid volume fraction and gas volume fraction in the CFGDL with varying PTFE content, and to further understand the effect of PTFE content on the mass transport in PEMFCs.

6.2. Experimental

6.2.1 Membrane electrode assembly (MEA) fabrication

PE-704 carbon paper (SGL, SIGRATHERM[®] paper) with the specific area density of 4.1 g cm⁻² and 0.3 mm in thickness, which has more macro-porous structure, was chosen as the electrode backing. Vulcan XC-72R carbon powder (Cabot Co.) was used as the electrically conductive filler and PTFE (60 wt. %, Aldrich) was used as the binder. E-TEK 20 wt.% Pt/C catalyst was used to prepare the hydrophobic-type catalyst layer where the Pt loading is 0.4 mgcm⁻². The Nafion112 was used to in the MEA for all investigated samples. The preparation procedure for making CFGDL, electrode with CFGDL and MEA is reported in Section 3.1. To study the effect of PTFE on the physical properties of CFGDL and cell performance, a set of CFGDLs with a fixed carbon loading (6 mg cm⁻²) was prepared by varying the PTFE contents from 10 to 60%.

6.2.2 Characterization

Pore size and distribution of the GDL were measured by a Mercury intrusion porosimetry (MIP) (Autopore III 9420, Micromeritics Inc.). The working principle of MIP has been described in detail in Section 3.3.6. In this study, the surface tension and contact angles of mercury used in the calculations of pore size, pore volume and pore volume distribution were 0.48 Nm⁻¹ and 130°, respectively [Uchida, 1995].

The hydrophilic properties of the GDL as a function of PTFE content was measured by the water uptake as described in Section 3.3.7. The water uptake of GDL is referred to the liquid water volume fraction in the sample and is expressed as:

$$\varepsilon_l = \frac{W_{water} / \rho_w}{V_{GDL}} \quad (6-2)$$

where W_{water} is the weight of liquid water contained in the GDL, ρ_w is the density of water, and V_{GDL} is the geometric volume of the GDL. In order to measure the W_{water} , the GDL was first dried in oven at 105 °C for 4 hr to obtain its dry weight W_{dry} , and then the dried GDL was immersed in the boiling water for 2 hr to obtain the corresponding wet weight W_{wet} . The weight of water, W_{water} , is obtained from the difference of the wet and dry weights of the sample, $W_{wet} - W_{dry}$. This procedure was repeated until the constant weight of liquid water contained in the GDL was obtained. Before weighing, the sample was taken out from the water and its surface water was dried by a tissue paper (this step was carried out as quickly as possible to avoid weighing errors). The procedure was repeated to obtain a constant W_{water} .

The microstructure of GDL was examined with a field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL Japan) operated at 5 kV as reported in Section 3.3.5.

Single cells with electrode area of 5 cm² and mesh flow field were used in the evaluation of the electrode performance. Steady state polarization was conducted on each sample. The cell performance was measured at 60 °C for H₂/O₂ and 80 °C for H₂/air under 1.5 bars on both anode and cathode. The hydrogen gas humidification was set at 5 °C higher than the cell temperature. In the case of H₂/O₂ test system, dry O₂ was used as oxidant and the flow arrangement was in the counter-flow manner. The gas flow rates are kept at a fixed stoichiometry (1.15 times stoichiometric for H₂ and 2 times stoichiometric for O₂) under a current density of 1 Acm⁻². When using air as the oxidant, reactants flows were arranged in co-flow manner and air humidification was set at 5 °C lower than the cell temperature. The gas flow rates were kept at 1.15 times stoichiometric for H₂ and 2.5 times stoichiometric for air

under a current density of 1 A cm^{-2} . The experiments were carried out using Arbin electronic load system.

6.3. Results and discussion

6.3.1 SEM and FESEM analysis

The macro-structure and submicron-structure of the GDL was characterized by using a scanning electron microscopy (SEM) and a field emission scanning electron microscopy (FESEM), respectively. Fig.6-1 shows the SEM/FESEM images of pure PTFE film and PTFE treated carbon paper. The PTFE film exhibits network structures in its micro-morphology with diameter of the pore in the network being around $1 \mu\text{m}$ and the size of knot being around $0.2 - 0.5 \mu\text{m}$ in diameter (Fig.6-1a). The PTFE treated carbon paper has a non-woven structure with many open and large pores (Fig.6-1b). When introducing carbon/PTFE filler into the carbon paper, the open and large pores are filled with the carbon/PTFE filler (Fig.6-2). However, the gap/void between the carbon fiber and carbon/PTFE agglomerates exists in the structure. The PTFE network structure associated with carbon particles is found in the carbon/PTFE filler as shown in Fig.6-3. A little loose structure with a higher PTFE content (40%) (Fig.6-3b), and a slightly dense structure with a lower PTFE content (10%) (Fig.6-3c) are observed. This indicates that the carbon particles mixed with PTFE also builds up the network structure (Fig.6-3a), which would be beneficial to the gas diffusion and water management in the GDL. The higher the PTFE content in the filler, the more the networks in the GDL will be. The insufficient PTFE in the carbon filler like 10% of PTFE would cause more carbon particles to be piled up in the structure. However, an excessive PTFE content like 60% of PTFE would increase the bulk resistance of CFGDL and contact resistances between GDL and catalyst layer/flow field plate as investigated in Chapter 5.

Fig. 6- 1 The SEM/FESEM images of (a) pure PTFE film and (b) PTFE treated carbon paper

Fig. 6- 2 The cross-section SEM image of carbon paper after embedding carbon/PTFE filler

Fig. 6- 3 Micro-structure of carbon/PTFE filler on the FESEM observation, (a) carbon/PTFE (40% PTFE content) network in the amplified 30,000 times (b) carbon/PTFE (40% PTFE content) network in the amplified 10,000 times (c) structure of carbon/PTFE filler with 10% PTFE content in the amplified 10,000 times

6.3.2. Effects of the PTFE content on the pore volume distribution in the gas diffusion layer

Generally, the GDL is treated with PTFE rendering its hydrophobicity. The degree of hydrophobicity is dependent on the amount of PTFE adding to GDL [Wang, 2003]. As investigated by FESEM in Section 6.3.1, the pore size distribution is affected by changing the PTFE content (Fig.6-3). MIP is a quantitative method to evaluate the pore size distribution and porosity of porous media. Fig.6-4 shows the pore distribution of the GDL with various PTFE contents obtained from mercury intrusion measurements. The cumulative pore volume decreases with the increasing PTFE content in GDL (Fig.6-4a), indicating that there will be the significant effect of PTFE on the porosity of the carbon-filled GDL. The pore size distribution in Fig.6-4b is symmetrical except for the case with PTFE content of 10%. The pore size distribution displays bimodal pore structure. The two peaks are located at the pore diameters of about $2\mu\text{m}$ and $30\mu\text{m}$. A boundary separating the two distinctive pore groups is at the

pore diameter of 10 μm . The pores with diameters of less than 10 μm are the primary pores, and larger than 10 μm the secondary pores. In the case of low PTFE content, there are multi-peaks in the primary pore region (the locations at 0.03 μm , 0.2 μm and 0.6 μm). As the PTFE content increases, the nano-sized pores start to disappear when the PTFE contents increase to 40%. It is believed that the primary pores are corresponding to space within the carbon agglomerates/PTFE networks (Fig.6-3) and the gap/void between the carbon fiber and carbon/PTFE agglomerates (Fig.6-2), while the secondary pores are corresponding to open space, coarse cracks on the surfaces. As shown in Fig.6-4b, the GDLs with different PTFE content show the similar pore size distribution in the secondary pore range, but significant differences are found for primary pore range. The nano-sized pores at ca. 35 nm and 0.2 μm in the primary pore size region may be attributed to the space within carbon agglomerate and thus are significantly affected by the PTFE content. It can be explained that the PTFE networks, which might separate carbon particles from agglomerates, would be formed in the structure with increasing in PTFE content so that the carbon agglomerates would be reduced.

Fig. 6-5 shows the changes in the ratio of pore volume at a certain pore size range to the geometric volume of GDL (referred as the local porosity) total porosity and average pore diameter as a function of PTFE content. It can be clearly seen that the total porosity of CFGDL associated with the local porosity in the pore size range of $< 1 \mu\text{m}$ decreases with the increase of PTFE content. The PTFE content has a little impact on the local porosity in the range over 10 μm , while the PTFE content of 40% presents the maximum porosity in the pore size range of 1 – 10 μm (Fig.6-5a). It indicates that the change of PTFE content in the structure of GDL does not affect the local porosities in the secondary pore region but would affect the nano-sized pore

distribution. However, the change of PTFE content in the structure of GDL does not affect the average pore diameter in the primary pore region but significantly affects the average pore size in the secondary pore region.

Fig. 6- 4 The effect of PTFE contents on (a) the cumulative volume and (b) pore size distribution

Fig. 6- 5 The effect of PTFE content in the CFGDL structure on (a) total and local porosities, (b) average pore size in each pore size region

6.3.3 GDL hydrophobicity / wetting analysis

Hydrophobic/wetting property of GDL was rarely reported in the literatures. This property is believed to be an important parameter for two-phase flow and transport within a GDL, often tailored to a specific cell design, and must be measured and correlated to the cell performance. Typically, this involves the measurement of contact angle on the surface by either a Sessile drop method or Wilhelmy method.

The contact angle θ , defined as the angle between the liquid-gas interface and the solid surface measured at the triple point where all three phases intersect, is a quantitative measure of the wetting of GDL by a liquid. A hydrophilic surface has a contact angle of less than 90° , whereas a hydrophobic surface has a contact angle of greater than 90° .

In this study, the contact angle of a CFGDL was measured based on Wilhelmy method [Mathias et al., 2003]. The CFGDLs have the same surface on both sides, which make contacts with the liquid in the measurement. Fig.6-6 shows the effect of PTFE content in CFGDL on the measured contact angle (disregard to the effects of surface roughness and porosity). It is clear that the PTFE content significantly affects the contact angle of CFGDL in particular with low PTFE content. The contact angle increases sharply with increasing PTFE content from 10% to 30% and nearly maintains a constant value from 40% to 60%. The threshold value is 40% of PTFE in CFGDL. Wang [2004] suggested that high contact angle is beneficial to the water removal.

Fig. 6- 6 The effect of PTFE content in CFGDL on the contact angle at 25 °C

The intrinsic contact angle for the hydrophobic coating (PTFE) is about 108° when measured the water droplets on flat and smooth surface [Nam and Kaviani, 2003]. Hydrophobic surfaces with a significant roughness exhibit super-hydrophobicity, with a measured contact angle ($> 135^\circ$) larger than the intrinsic contact angle [Mathias et al., 2003]. With respect to the effect of the surface roughness and porosity of GDL, the measured contact angles can be corrected using the Cassie-Baxter equation for porous surfaces modified for surface roughness [Gositick et al., 2006]:

$$\cos \theta_{c,m} = b f_1 \cos \theta_c - f_2 \quad (6-3)$$

Where $\theta_{c,m}$ is the measured contact angle, b the ratio of actual area of contact between the droplet and the solid portion of surface to the projected area ($b = \pi/2$ for cylinders and $b = \pi$ for spheres, thus $b = 0.75\pi$ for the mixed composite of carbon agglomerate and carbon fiber based on the image as shown in Fig.6-2), and f_1 and f_2 the fractions of the GDL surface occupied by solid and void, respectively [Gositick et al., 2006]. Thus, the f_1 is equal to $1 - f_2$ where f_2 is referred to the local porosity of CFGDL with pore sizes larger than $1 \mu\text{m}$, which are corresponding to the gap/void between the carbon fiber and carbon/PTFE agglomerates, open space, and coarse cracks on the surfaces. The results of this analysis are given in Table 6-1. It can be seen that the corrected contact angles are much smaller than those of the measured contact angles; the corrected contact angle of CFGDL with 10% of PTFE content is about 80° (less than 90°) indicating that the intrinsic surface of such a GDL would be hydrophilic.

Table 6- 1 Measured and corrected contact angles of CFGDLs with varying PTFE content

PTFE content (%)	Measured contact angle, $\theta_{c,m}$	f_1	f_2 (local porosity with the pore size $> 1 \mu\text{m}$)	Corrected contact angle, θ_c
10	108.7	0.536	0.464	83.5
20	126.3	0.517	0.483	95.2
30	138.9	0.507	0.493	102.6
40	144.4	0.499	0.501	105.4
50	144.5	0.518	0.482	105.8
60	145.8	0.533	0.467	106.6

6.3.4. Water uptake of GDL

As is known, the current proton exchange membranes for PEMFC such as Nafion require external humidification in order to exhibit good proton conductivity. Water is produced from the oxygen reduction reaction on the cathode. Thus, the cathode in the PEM fuel cell is susceptible to flooding, i.e., filling of pores with liquid water, especially at high current densities. Although the introduction of hydrophobic polymer such as PTFE could reduce the retention of liquid water, in the GDL quantitative determination of water retention in the electrode especially GDL (thicker compared to catalyst layer) is still important. Lim and Wang [2004] thought that the measurement of GDL contact angle is a practical way to determine the water flooding of GDL.

In this study, a direct measurement of water uptake of GDL is studied in detail. It is believed that this method effectively and quantitatively measures the water uptake, namely the liquid retention of GDL, which is another important parameter for two-phase flow and transport within a GDL. Fig.6-7 shows the water uptake (the ratio of liquid water volume to geometric volume of the GDL) of GDL with different PTFE

content. With increasing PTFE content from 10% to 30%, the water uptake in GDL drops sharply from 34% to 5.8% and then decreases slowly with further increase of PTFE content. This indicates that the liquid retention in the GDL decrease significantly with the increase in the PTFE content and become constant once the PTFE content is increased to above 30-40%. This may be due to the gradual formation of the PTFE networks in the GDL structures with increasing PTFE and the threshold content for the formation of the PTFE network appears to be at 40%.

Fig. 6- 7 The water uptake (the ratio of water volume to geometric volume of the GDL) of GDL with different PTFE content

In fact, the water uptake can be referred to the liquid volume fraction ε_l [Litster and Djilali, 2005] in the GDL. For porous media in which the void space is occupied by two-phases, the total porosity ε is divided into the liquid ε_l and gas ε_g volume fractions. The liquid saturation s_l , a parameter for analysis of the extent of water occupying the space in the porous media, is defined as the liquid volume fractions ε_l

divided by the open pore volume ε . This relationship is expressed in the following equation:

$$\varepsilon_l + \varepsilon_g = 1 \text{ and } s_l = \frac{\varepsilon_l}{\varepsilon} \quad (6-4)$$

From the Eq.6-4, a porosity correction model that simplifies the two-phase problem by neglecting the transport of liquid water can be established. The volume fraction open to the gas phase can be expressed as:

$$\varepsilon_g = \varepsilon(1 - s_l) \quad (6-5)$$

Fig.6-8 shows the plots of the total porosity (ε), the liquid volume fraction (ε_l) and the gas volume fraction (ε_g) as a function of the PTFE content. The gas volume fraction ε_g , increases rapidly with increasing PTFE content from 10% to 30%, showing the plateau value between 30% and 40%, and then decreases gradually with further increasing PTFE content up to 60%. The high gas volume fraction between 30% and 40% would be beneficial to the mass transport of reactants through CFGDL at high current density operation of a fuel cell.

In this study, the water saturation ($s_l = \varepsilon_l / \varepsilon$), which is obtained by computing from the value of water uptake, i.e., the liquid retention in GDL, should be referred to as the immobile saturation s_{im} (also as the irreducible saturation) [Litster and Djilali, 2005]. It is believed that the immobile saturation would be related to the extent of water flooding of GDL. Fig.6-9 shows the immobile saturation of CFGDL as a function of PTFE contents. It can be seen that the significant dependence of immobile water saturation is on the PTFE content in CFGDL.

Fig. 6- 8 The plots of the total porosity, the fraction of hydrophilic pore and the fraction of hydrophobic pores as a function of the PTFE content

Fig. 6- 9 The plots of the water saturation, the volume fraction of liquid within open pores in CFGDL, as a function of the PTFE conten

6.3.5 Fuel cell performance

Fig.6-10a shows the polarization curves of the cells with different PTFE contents in the GDL of cathodes, measured at 60 °C in H₂/O₂. It is apparent that the PTFE content of the GDL affects the polarization performance of the cell in the ohmic and mass transport control polarization regions, but has little effect in the activation control region. The highest power density was obtained from the cell with 30% of PTFE in GDL as seen in Fig.6-10b. This corresponds to a distribution of 5.8% of the liquid volume fraction and 62% of the gas volume fraction in the GDL porous structure. A low PTFE content of 10% (corresponding to a distribution of 34% of the liquid volume fraction and 37% of the gas volume fraction) or a high PTFE content of 60% (corresponding to a distribution of 3.1% of the liquid volume fraction and 55% of the gas volume fraction) would lead to a reduced cell performance.

Fig. 6- 10 (a) the polarization curves and (b) the plot of power density vs. current density of the cells obtained at 60 °C with different PTFE contents in the CFGDL of cathodes in H₂/O₂

Fig.6-11a shows the polarization curves of the cells with different PTFE contents in the GDL of cathodes, measured at 80 °C under H₂/air. Similar to that using H₂/O₂ as reactants, the PTFE content of the GDL primarily affects the polarization performance of cells in the ohmic and mass transport control polarization regions.

However, different from that in the H_2/O_2 system, the polarization curves departure from linear regions at lower current densities, indicating the increased dominance of the gas diffusion limitation. The highest power density of the cell was observed with 40% of PTFE in GDL (Fig.6-11b). This corresponds to a distribution of 3.8% of the liquid volume fraction and 62% of the gas volume fraction in the GDL porous structure.

Fig. 6- 11 (a) the polarization curves and (b) the plot of power density vs. current density of the cells obtained at 80 °C with different PTFE contents in the CFGDL of cathodes in H_2 /air

In PEM fuel cell, the major mass transport losses are associated with the transport of O_2 from the flow field plate to the GDL/catalyst layer interface through GDL and then to the active sites, the transport of the water from the GDL/catalyst layer interface to the flow field plate through GDL at the cathode and the transport of proton in the membrane. In this investigation, it is considered that the mass transport losses with varying PTFE content in the CFGDLs are due mainly to the transport of O_2 and water in the CFGDL. It is worth noting that, in Fig.6-10a, the polarization curves of the cells using CFGDLs with PTFE content of more than 30% have maintained the linear region at current density more than 2000 mA/cm^2 ; while the polarization curves of cell using CFGDLs with 10% PTFE departed from the linearity at about 1600 mA/cm^2 . The departure of polarization curve from linear regions in the

high current density range is considered to be due to the concentration over-potential. In this region, the loss due to mass diffusion limitation is dominant. However, the mass transport limitation in the electrodes caused by reactants (pure H₂ and O₂) should not occur earlier as expected, even if the gas phase at the cathode is saturated with water vapor.

6.3.6 Flooding analysis

The aforementioned phenomena can be studied by a model analysis if the catalyst layer is assumed to be infinitesimally thin and the cathode liquid saturation is uniform. Oxygen is transported from the cathode gas channel to the cathode GDL via convection, and then diffuses through the cathode GDL to the catalyst layer. In this derivation, convective transport of oxygen across porous GDL is neglected. When the catalyst layer is assumed to be infinitesimally thin, the electrochemical reaction of oxygen reduction is governed by the Butler-Volmer equation, and because the cathode kinetics is sufficiently sluggish, it can be expressed by Tafel kinetics, *i.e.*,

$$i = a_e i_0^{ref} \frac{C_{O_2}}{C_{O_2}^{ref}} \exp\left(-\frac{\alpha_c n F}{RT} \eta\right) \quad (6-6)$$

where a_e is the electrochemically active surface area (*ESA*) with units of cm²cm⁻²; i_0^{ref} the reference exchange current density with units of Acm⁻²; C_{O_2} and $C_{O_2}^{ref}$ the dissolved oxygen concentration in the catalyst layer and reference oxygen concentration with units of molcm⁻³, respectively.

The reference exchange current density for oxygen reduction in Nafion is given by the Parthasarathy et al. [1992] correlation:

CHAPTER 6 Effect of PTFE Content on the Mass Transport in the Gas Diffusion Layer for PEMFCs

$$\log(i_{0,ref}) = 3.507 - \frac{4001}{T} \quad (6-7)$$

The dissolved oxygen concentration in the catalyst layer can be determined from the solubility of oxygen gas in Nafion polymer using the Henry's law:

$$C_{O_2} = \frac{p_{O_2}}{H_{O_2}} \quad (6-8)$$

where p_{O_2} is the partial pressure (atm) of oxygen at the gas diffusion layer/catalyst layer interface, and H_{O_2} is the Henry's constant for oxygen gas dissolution in the Nafion polymer (atm cm³/mol). The Henry's constant is calculated from an empirical correlation [D.M. Bernardi, 1991]:

$$\ln(H_{O_2}) = -\frac{666}{T} + 14.1 \quad (6-9)$$

When air is used as the oxidant, p_{O_2} can be calculated using the following equation as derived in Appendix I,

$$p_{O_2} = P_t \left[1 - x_w^{sat} - x_{N_2}^{ch} \exp\left(\frac{35i\delta_d}{(\varepsilon_g/\tau)T^{0.832}}\right) \right] \quad (6-10)$$

where $x_{N_2}^{ch}$ and x_w^{sat} ($= p_w^{sat}/P_t$, p_w^{sat} is the saturated pressure of water vapor) are the mole fractions of nitrogen in the channel and saturated water vapor, respectively; P_t the total pressure on the cathode channel, δ_d the thickness of GDL, ε_g the gas volume fraction represented by the equation $\varepsilon_g = \varepsilon(1 - s_l)$ and τ the tortuosity factor (ranging from 2 to 4 for randomly oriented pores, 3.5 is used in this study). The liquid saturation s_l should include immobile water saturation s_{im} and the fraction of liquid

water flux within pores which is termed the mobile water saturation s_m , i.e.,

$s_l = s_{im} + s_m$. Then, the Eq.6-10 can be rewritten as,

$$p_{O_2} = P_t \left[1 - x_w^{sat} - x_{N_2}^{ch} \exp \left(\frac{35i\delta_d}{[\varepsilon(1 - s_{im} - s_m) / \tau] T^{0.832}} \right) \right] \quad (6-11)$$

A similar development for the pure oxygen used as an oxidant yields the equations (as described in Appendix I),

$$p_{O_2} = p_w^{sat} \left[\frac{1}{\exp \left(\frac{503i\delta_d}{(\varepsilon_g / \tau) T^{1.334}} \right) \cdot x_w^{ch}} - 1 \right] \quad (6-12)$$

and

$$p_{O_2} = p_w^{sat} \left[\frac{1}{\exp \left(\frac{503i\delta_d}{[\varepsilon(1 - s_{im} - s_m) / \tau] T^{1.334}} \right) \cdot x_w^{ch}} - 1 \right] \quad (6-13)$$

Combining equations (6-6), (6-8) and (6-11), the cathode overpotential using air as an oxidant as a function of cell temperature, total pressure at the cathode, liquid saturation in the GDL, and the current density can be given by

$$\eta_c = -\frac{RT}{\alpha_c nF} \cdot \ln \left\{ \frac{iC_{O_2}^{ref} H_{O_2}}{ai_0^{ref} P_t \left[1 - x_w^{sat} - x_{N_2}^{ch} \exp \left(\frac{35i\delta_d}{[\varepsilon(1 - s_{im} - s_m) / \tau] T^{0.832}} \right) \right]} \right\} \text{ for air } (6-14).$$

Combining equations (6-6), (6-8) and (6-13), the cathode overpotential using pure oxygen as an oxidant as a function of cell temperature, mole fraction of water vapour at the cathode channel, liquid saturation in the GDL, and the current density can be expressed as

$$\eta_c = -\frac{RT}{\alpha_c nF} \cdot \ln \left\{ \frac{iC_{O_2}^{ref} H_{O_2} x_w^{ch} \exp\left(\frac{503i\delta_d}{[\varepsilon(1-s_{im}-s_m)/\tau]T^{1.334}}\right)}{ai_0^{ref} p_w^{sat} \left[1 - x_w^{ch} \exp\left(\frac{503i\delta_d}{[\varepsilon(1-s_{im}-s_m)/\tau]T^{1.334}}\right)\right]} \right\} \text{ for O}_2 \quad (6-15)$$

Tables 6-2 and 6-3 summarise the physical and operating parameters for the model calculations. The characteristic parameters of electrode associated with GDLs, such as electrochemically active surface area (a_e), porosity of GDL (ε) and immobile liquid saturation (s_{im}) are based on the experimental results in this study.

In Fig.6-12, the cathode overpotential vs. current density is plotted for different liquid saturation values when using H₂ and air as reactants. It is seen that the cathode overpotential increases with increasing current density and increase in the liquid saturation of GDL results in an increase in cathode overpotential. The increase in the cathode overpotential with increasing liquid saturation is smaller for low current densities and becomes much higher at high current densities. This is attributed to the fact that at higher current densities, the cathode reaction rate is limited by the rate of oxygen transport to the reaction sites. However, in lower current densities the cathode reaction is controlled by activation losses; hence, the change in the cathode overpotential with increasing liquid saturation is not as high as at higher current densities. It is also clearly seen that the limiting current density is controlled by the amount of liquid water present in GDL. This indicates that the limitation of oxygen

transport due to liquid water is dominant in the cathode overpotential. Fig.6-13 shows the plot of the cathode overpotential vs. current density at a constant mobile liquid saturation in GDL with different PTFE content when using H_2 and air as reactants. It is seen that the cathode overpotential is significantly dependent on the PTFE content in GDL and decrease in the PTFE content in GDL results in an increase in cathode overpotential at the same mobile liquid saturation. This is attributed to the effect of the immobile liquid saturation in GDL, since decrease in the PTFE content in GDL results in an increase in the immobile liquid saturation in GDL as reported in Section 6.3.4. When using H_2 and O_2 as reactants, the cathode overpotential is little dependent on the PTFE content and no limitation of oxygen transport is observed in the range more than 20% (Fig.6-14). However, the PTFE content of 10% in GDL results in the limitation of oxygen transport. It is revealed that the GDL might be fully flooded by liquid water. It is in good agreement with the fact that the GDL with 10% PTFE content presents hydrophilic behavior and tally with the corrected contact angle of about 80° (less than 90°) as seen in Section 6.3.3. From the model analysis, it is clearly seen that the loss due to mass diffusion limitation in the electrode is seriously controlled by the water saturation of GDL at high current density. The appearance of mass transport limitation in the electrodes with the PTFE content of 10% at high current density, when using pure H_2 and O_2 as reactants, is attributed to the high immobile saturation of such a GDL.

Table 6- 2 Operating and physical parameters used in Eq. (6-14)

Parameters	Unit	Value
Reactants: H ₂ and air		
Cell pressure, P_t	atm (abs)	2.5
Cell temperature, T	K	353
Mole fractions of nitrogen in the channel, $x_{N_2}^{ch}$		0.684
Mole fractions of saturated water vapor, x_w^{sat}		0.187
Reference exchange current density for ORR in Nafion, i_0^{ref}	Acm ⁻²	1.488×10^{-8}
Reference oxygen concentration, $C_{O_2}^{ref}$ [Marr and Li, 1999]	molcm ⁻³	1.2×10^{-6}
Henry's constant for oxygen gas dissolution in the Nafion polymer, H_{O_2}	atm cm ³ /mol	2.0×10^5
Gas constant, R	Jmol ⁻¹ K ⁻¹	8.3144
Faraday constant, F	Cmol ⁻¹	96487
Number of electron, n		2
Cathode transfer coefficient, a_c		0.5
Thickness of GDL, δ_d	cm	0.03
Tortuosity factor, τ		3.5

Table 6- 3 Operating and physical parameters used in Eq. (6-15)

Parameters	Unit	Value
Reactants: H ₂ and O ₂		
Cell pressure, P_t	atm (abs)	2.5
Cell temperature, T	K	333
Saturated pressure of water vapor, p_w^{sat}	atm	0.196
Mole fractions of water vapor, x_w^{ch} (an arithmetic mean of inlet and outlet mole fractions of water vapor)		0.0392
Reference exchange current density for ORR in Nafion, i_0^{ref}	Acm ⁻²	3.1×10^{-9}
Reference oxygen concentration, $C_{O_2}^{ref}$ [Marr and Li, 1999]	molcm ⁻³	1.2×10^{-6}
Henry's constant for oxygen gas dissolution in the Nafion polymer, H_{O_2}	atm cm ³ /mol	1.8×10^5
Gas constant, R	Jmol ⁻¹ K ⁻¹	8.3144
Faraday constant, F	Cmol ⁻¹	96487
Number of electron, n		2
Cathode transfer coefficient, a_c		0.5
Thickness of GDL, δ_d	cm	0.03
Tortuosity factor, τ		3.5

Fig. 6- 12 Cathode overpotential vs. current density for different mobile liquid saturation in GDL with PTFE content of 40% when using H₂ and air as reactants

Fig. 6- 13 Cathode overpotential vs. current density for different PTFE content in GDL ($s_m = 0.6$) when using H₂ and air as reactants

Fig. 6- 14 Cathode overpotential vs. current density for different PTFE content in GDL ($s_m = 0.738$) when using H_2 and O_2 as reactants

CHAPTER 7 A Macro-model for Analysis of Possibility of the Self – humidifying Operation in PEMFCs

7.1 Introduction

As acknowledged, to achieve stable and high cell performances for PEFC there must be sufficient water content in the polymer electrolyte. The proton conductivity is directly proportional to the water content. However, there must not be too much water that causing electrode flooding, thus blocking the pores in the electrodes for gas diffusion. A good water balance is therefore needed. The mechanisms of membrane dehydration involve (i) electro-osmotic drag pulling water molecules from anode to cathode between 1 (gas vapor equilibrated membranes) and 2.5 (liquid water equilibrated membranes) water molecules are ‘dragged’ for each proton [Fuller and Newman, 1992; Zawodzinski et al., 1995; and Ise et al., 1999]; and (ii) loss of water to unsaturated fuel or air streams. The dry anode issue caused by the first mechanism “electro-osmotic drag” has been mentioned in the last chapter. The introduction of hygroscopic oxide (silica) into the catalyst layer of electrode and use of thin electrolyte membrane (high rate of water back-diffusion from the cathode to anode) can solve the dry anode issue. Understanding of the second mechanism is important for self-humidification fuel cell design. In PEFC, the water which forms at the cathode, ideally, should keep the electrolyte at the correct level of hydration. The key is to predict and control both water production and the water drag which directly proportional to the current, and the back diffusion of water from the cathode to the anode and the relative humidity (referred to water activity) on each side. Thus, running a fuel cell without external humidification should be possible by setting the air stoichiometry to a correct level so that the relative humidity of the exit air is about 100% and water balance within the cell is achieved. In this study, a new macro-model

for predicting the possibility of the self-humidifying operation in PEFC is developed based on the work reported by Chan et al. [2006] and Yu [2000]. The suitable range of operating temperatures and air stoichiometric number under different condition can be estimated using this model. The relationships between relative humidity of exit air/H₂ and air stoichiometric number under different water removal from the anode and membrane conductivity are also established.

7.2 Theoretical analysis

7.2.1 Model formulation

7.2.1.1 Relationship between relative humidity and air stoichiometric number

Based on Chan et al., the overall reaction in the H₂ (dry)/air PEM fuel cell can be expressed as:

In the equation,

$$u = \text{Sto}_\text{H} \quad (7-2),$$

$$v = \frac{\text{Sto}_\text{A} p_c}{2(p_c - RH_{in} p_{in}^{sat})} \quad (7-3),$$

$$w = \frac{\text{Sto}_\text{A} RH_{in} p_{in}^{sat}}{2(p_c - RH_{in} p_{in}^{sat})} \quad (7-4)$$

and

$$x = 1 + \frac{\text{Sto}_\text{A} RH_{in} p_{in}^{sat}}{2(p_c - RH_{in} p_{in}^{sat})} \quad (7-5),$$

CHAPTER 7 A Macro-model for Analysis of Possibility of the Self-humidifying Operation in PEMFCs

$$y = \frac{\text{Sto}_A p_c}{2(p_c - RH_{in} p_{in}^{sat})} - \frac{1}{2} \quad (7-6),$$

$$z = \frac{\beta \text{Sto}_A p_c}{2(p_c - RH_{in} p_{in}^{sat})} \quad (7-7),$$

$$t = \text{Sto}_H - 1 \quad (7-8),$$

where Sto_H and Sto_A are the stoichiometric number of H_2 and air respectively; p_c the pressure of cathode side; RH_{in} the relative humidity of inlet air; p_{in}^{sat} , the saturated vapor pressure; and $\beta = 3.762$, which is the volume ratio of nitrogen to oxygen in the air.

Fig. 7- 1 Schematic diagram of mass balance of species in PEM fuel cell

If one assumes that the back diffusion of water is more dominant than the electro-osmotic drag causing net water transport from the cathode to the anode, then the mass balance for chemical species in Eq.7-1 in the PEM fuel cell can be described by the law of conservation of mass, as shown in Fig.7-1. It is assumed that the water generated by the electrochemical reaction in the fuel cell exists in the water vapor as an ideal gas. The relationship between the molar flux of species and the partial pressure can be expressed as:

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$$\frac{f \times x}{t} = \frac{p_{w,a}}{p_a - p_{w,a}} \quad (7-9)$$

and

$$\frac{(1-f) \times x}{y+z} = \frac{p_{w,c}}{p_c - p_{w,c}} \quad (7-10)$$

where, f is the ratio of the water removal from the anode to the total water including water carried by the inlet air and generated by the electrochemical reaction in the cell, with the range of $0 \leq f < 1$, in other words, f represents the net water flow rate through the membrane from the cathode to the anode, when the water flow rate from the cathode to the anode due to the back diffusion of water is equal to the water flow rate from the anode to cathode due to the electro-osmotic drag, the water transport through the membrane is at equilibrium and the net water flow rate is zero, in this case $f = 0$; p_a the pressure at the anode side; $p_{w,a}$ and $p_{w,c}$ the water partial pressure at anode and cathode, respectively.

And, the water partial pressure can be expressed as

$$p_{w,a} = \frac{fp_a[2(p_c - RH_{in}p_{in}^{sat}) + RH_{in}p_{in}^{sat}Sto_A]}{2(Sto_H - 1 + f)(p_c - RH_{in}p_{in}^{sat}) + fRH_{in}p_{in}^{sat}Sto_A} \quad (7-11)$$

and

$$p_{w,c} = \frac{(1-f)p_c[2(p_c - RH_{in}p_{in}^{sat}) + RH_{in}p_{in}^{sat}Sto_A]}{(1-2f)(p_c - RH_{in}p_{in}^{sat}) + [(1-f)RH_{in}p_{in}^{sat} + (1+\beta)p_c]Sto_A} \quad (7-12).$$

The relative humidity of the gases is defined as:

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$$RH = \frac{p_w}{p_T^{sat}} \quad (7-13)$$

where, the saturation pressure of the water vapor can be obtained from the following expression (Appendix 2),

$$p_T^{sat} = -0.03089 + 0.02451 \exp\left(\frac{T}{26.6731}\right) \quad (7-14),$$

and the unit of the p_T^{sat} is atm, and the unit of the cell temperature T is $^{\circ}\text{C}$.

Thus, the relative humidity of gases at the outlets of anode and cathode are:

$$RH_{out,a} = \frac{fp_a[2(p_c - RH_{in}p_{in}^{sat}) + RH_{in}p_{in}^{sat}\text{Sto}_A]}{[2(\text{Sto}_H - 1 + f)(p_c - RH_{in}p_{in}^{sat}) + fRH_{in}p_{in}^{sat}\text{Sto}_A]p_T^{sat}} \quad (7-15)$$

and

$$RH_{out,c} = \frac{(1-f)p_c[2(p_c - RH_{in}p_{in}^{sat}) + RH_{in}p_{in}^{sat}\text{Sto}_A]}{\{(1-2f)(p_c - RH_{in}p_{in}^{sat}) + [(1-f)RH_{in}p_{in}^{sat} + (1+\beta)p_c]\text{Sto}_A\}p_T^{sat}} \quad (7-16)$$

7.2.1.2 Relationship between the optimal temperature for fuel cell stable operation and air stoichiometric number

The humidity of the air in PEFC should be controlled so that the air is dry enough to evaporate the product water but not so dry that it dries too much – it is essential that the electrolyte membrane retain high water content. It is believed for stably operating a PEFC the humidity of exit air in the cathode should be above 80% to prevent excessive drying, but must be below 100%, or liquid water would be condensed in the electrodes [Larminie & Dicks, 2003, fuel cell explained 2nd]. Thus, combined Eq.7-14 with Eq.7-15 or Eq.7-16, the optimal cell temperature for the stable operation of PEM fuel cell can be estimated by:

$$\begin{aligned}
 & 26.6731 \ln \left\{ \frac{40.8 f p_a [2(p_c - RH_{in} p_{in}^{sat}) + RH_{in} p_{in}^{sat} \text{Sto}_A]}{[2(\text{Sto}_H - 1 + f)(p_c - RH_{in} p_{in}^{sat}) + f RH_{in} p_{in}^{sat} \text{Sto}_A]} + 1.26 \right\} \leq T_{h,a} \leq \\
 & 26.6731 \ln \left\{ \frac{51 f p_a [2(p_c - RH_{in} p_{in}^{sat}) + RH_{in} p_{in}^{sat} \text{Sto}_A]}{[2(\text{Sto}_H - 1 + f)(p_c - RH_{in} p_{in}^{sat}) + f RH_{in} p_{in}^{sat} \text{Sto}_A]} + 1.26 \right\}
 \end{aligned}
 \tag{7-17}$$

and

$$\begin{aligned}
 & 26.6731 \ln \left\{ \frac{40.8(1-f)p_c [2(p_c - RH_{in} p_{in}^{sat}) + RH_{in} p_{in}^{sat} \text{Sto}_A]}{(1-2f)(p_c - RH_{in} p_{in}^{sat}) + [(1-f)RH_{in} p_{in}^{sat} + (1+\beta)p_c] \text{Sto}_A} + 1.26 \right\} \leq T_{h,c} \leq \\
 & 26.6731 \ln \left\{ \frac{51(1-f)p_c [2(p_c - RH_{in} p_{in}^{sat}) + RH_{in} p_{in}^{sat} \text{Sto}_A]}{(1-2f)(p_c - RH_{in} p_{in}^{sat}) + [(1-f)RH_{in} p_{in}^{sat} + (1+\beta)p_c] \text{Sto}_A} + 1.26 \right\}
 \end{aligned}
 \tag{7-18}$$

Note that the highest cell temperature should be the smaller value between the $T_{h,a}$

and $T_{h,c}$.

7.2.1.3 Relationship between the conductivity of membrane and relative humidity

The conductivity of Nafion membrane is significantly dependent upon the water content in the membrane. The relationship between the conductivity and water content can be expressed by [Springer et al., 1991]:

$$\kappa(\text{Scm}^{-1}) = (0.005139\lambda - 0.00326) \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T(K)} \right) \right] \tag{7-19}$$

where λ is the water content of the membrane which is determined by the activity of water vapor (referred to relative humidity (RH) in the cell) at the electrode/membrane interface, assuming equilibrium. It can be expressed as:

$$\lambda_{(30C)} = 0.043 + 17.81RH - 39.85RH^2 + 36.0RH^3 \text{ for } 0 \leq RH \leq 1 \tag{7-20}$$

It was suggested that the 30 °C data could be applied to membrane equilibrium with water vapor at 80 °C. Thus, the relationship between the membrane conductivity and relative humidity of water vapor at different temperature can be established.

7.2.2 Operating condition and parameters

In this study, it is assumed that the rate of water transport through the membrane is fast as the thin membrane Nafion 112 (50µm in thickness) was used; all the heat transfer in the fuel cell is ignored; the water in the fuel cell at both anode and cathode is discharged from the cell in the water vapor state. The fuel cell operates under the same gas pressure at both anode and cathode sides. The dry pure hydrogen flux is introduced into the fuel cell. The operating condition and parameters are listed in Table 7-1.

Table 7- 1 Parameters for model calculation

Parameter	Value
Air temperature at the inlet, T	25 °C
Relative humidity of air at the inlet, RH_{in}	adjustable
Saturation pressure of water at 25 °C, p_{in}^{sat}	0.03128 atm
The volume ratio of N ₂ to O ₂ in air, β	3.762
The gas pressure at the cathode, p_c	1.1 atm
The gas pressure at the anode, p_a	1.1 atm

7.3 Results and discussion

7.3.1 Relationship between relative humidity and stoichiometric number of air

Fig.7-2 shows the relationship between stoichiometric number of air and relative humidity of exit air at $f=0$ and $RH_{in,c}=0$. It can be seen that the relative humidity $RH_{out,c}$ on the cathode side is significantly dependent on the air stoichiometric

number and the fuel cell operating temperature. $RH_{out,c}$ decreases significantly with increasing air stoichiometric number at a given temperature or increasing the cell temperature at a given stoichiometric number. The decrease in $RH_{out,c} (= p_w / p_T^{sat})$ with increasing air stoichiometric number is due to the decrease of the mole fraction (x_w) of water in the exit air with increasing the air stoichiometric number, causing the decrease of water partial pressure ($p_w = P_t x_w$); and decrease in $RH_{out,c} (= p_w / p_T^{sat})$ with increasing cell temperature is due to the increase of saturated pressure of water (p_T^{sat}).

According to Larminie & Dicks [2003] who suggested the suitable range of $R_{out,c}$ for stable fuel cell operation, the results in Fig.7-2 show that when the curves of $R_{out,c}$ vs. Sto_A fall in the shaded region ($0.8 < RH_{out,c} \leq 1$, water vapor phase), the fuel cell under study could operate stably. Above the shaded region, the water would be condensed in the cell causing electrode flooding at cathode side. Below the shaded region, the membrane would be too dry to function properly. It was found that there is a possibility to operate a fuel cell at about 60 °C with dry reactants if an appropriate range of air stoichiometric number ($2.15 \leq Sto_A < 2.71$) is used. The introduction of nano-size hygroscopic agent such as silica in anode catalyst layer was proven to be useful for stable cell operation at elevated temperatures [Han et al., 2006]. Although the curves of $R_{out,c}$ vs. Sto_A pass through the shaded region and fall in $1.27 \leq Sto_A < 1.64$ at 70 °C and in $3.58 \leq Sto_A < 4.5$ at 50 °C, a lower stoichiometric number of air will cause a poorer fuel cell performance due to the reduced average oxygen concentration, hence, increased concentration overpotential; while a higher stoichiometric number of air will result in decreased air utilization thus increasing the

parasitic energy. The air stoichiometric number is normally chosen within the range of 2 – 4, which is dependent on a fuel cell design. Judging from the above findings and requirements, it is appropriate to operate a fuel cell stack with dry reactants at temperature not exceeding 60 °C.

Fig.7-3 shows the effect of the relative humidity of inlet air on the relative humidity of the exit air at the cathode with varying air stoichiometric number at a cell temperature of 60 °C. It can be found that the relative humidity of exit air is almost independent on the relative humidity of inlet air. This is because the water vapor carried by the inlet air stream (even if the air is saturated with water) at the ambient condition (25 °C) is too little to have significant impact on the relative humidity of the exit air compared to the water generated at the cathode. This result indicates that there is possibility for PEM fuel cells, especially a small fuel cell stack with “dead-end” hydrogen flow channel design, to operate with either a wet or dry air at ambient condition without external humidification assuming that the relative humidity at the anode is saturated with water vapor.

Fig. 7- 2 The relationship between stoichiometric number of air and relative humidity of exit air at $f = 0$ (equivalent to H_2 “dead end”) with $RH_{in} = 0$

Fig. 7- 3 The effect of the relative humidity of inlet air on the relative humidity of the exit air at the cathode ($f = 0$, $T_{\text{cell}} = 60\text{ }^{\circ}\text{C}$ and $T_{\text{in,A}} = 25\text{ }^{\circ}\text{C}$)

When f value is larger than zero ($f > 0$), it means that the net water flow through the membrane from the cathode to the anode will occur and part of the water generated at the cathode arising from reactions will be removed at the anode. There is a possibility for the hydrogen stoichiometric number Sto_H to be larger than 1 when reformed gas is used as the fuel. In this case, the relative humidity at the anode will also affect the stability of a fuel cell operation. As such, it is likely that the anode would be over saturated with water at the anode causing anode flooding. Thus, the relative humidity at the anode would be dependent on the f value and the hydrogen stoichiometric number. The relationships between the relative humidity (for both the cathode and the anode) and air stoichiometric number are shown in Fig.7-4 and 7-5 (contour plots) with varying the f value at the hydrogen stoichiometric number of 1.25 and 1.5, respectively. In Fig.7-4 and 7-5, the horizontal contour lines represent the constant relative humidity line on the cathode side and the vertical contour lines represent the constant relative humidity line on the anode side. The stable operating regions for

working fuel cells with varying the air stoichiometric number Sto_A and f value under different cell temperatures and inlet air conditions are marked as shaded region. At low temperature, the stability operating region is located in the area with a high Sto_A value and a small f value, while at a high temperature the stability of operating region is located in the area with a low Sto_A value and a large f value. However, too large or too small air stoichiometric number Sto_A is not practical for a fuel cell operation as mentioned previously. Thus, the reasonable air stoichiometric number should match with the cell temperature of $50\text{ }^{\circ}\text{C} - 60\text{ }^{\circ}\text{C}$. The f value is referred to the net water transport through the membrane from the cathode to the anode and its value is mainly dictated by the properties of the electrolyte membrane (such as thickness, equivalent weight, etc.), the water concentration gradient across the membrane and degree of electro-osmotic drag for an operating fuel cell with dry reactants. Janssen and Overvelde [2001] suggested that a thinner membrane with similar boundary conditions result in larger water gradients across the membrane and a membrane with higher equivalent weight (i.e., lower water content) would increase the net water transport from the cathode to the anode due to a smaller electro-osmotic drag in the membrane. Thus, an appropriate f value could be “tuned” with careful selection of the membrane property with desired properties. For Nafion112, the f value is about 0.02 – 0.09 with dry reactants on both the cathode and the anode based on the work done by Janssen and Overvelde. In general, a higher f value would improve the hydration of membrane when using dry gases, even at elevated cell temperatures. The effect of the hydrogen stoichiometric number on stable operation of a fuel cell is summarized in Table 7-2, in which the data are extracted from Fig.7-4 and 7-5. It can be found that a higher f value is required to maintain the stable operation for a fuel cell at higher hydrogen stoichiometric number.

(a)

(b)

(c)

(d)

Fig. 7- 4 The effect of the stoichiometric number of air and f value on the relative humidity of exit air and H_2 at $Sto_a = 1.25$ and the temperature of (a) 40°C , (b) 50°C , (c) 60°C and (d) 70°C

(a)

(b)

(c)

(d)

Fig. 7- 5 The effect of the stoichiometric number of air and f value on the relative humidity of exit air and H_2 at $Sto_a = 1.5$ and the temperature of (a) $40\text{ }^{\circ}\text{C}$, (b) $50\text{ }^{\circ}\text{C}$, (c) $60\text{ }^{\circ}\text{C}$ and (d) $70\text{ }^{\circ}\text{C}$

Table 7- 2 The ideal operating conditions for fuel cell stable operation

Operating conditions		Sto_A	f value
$RH_{in,c} = 0.5$	$T_{cell} = 40\ ^\circ C$	6 – 8	0.017 – 0.02
$Sto_H = 1.25$	$T_{cell} = 50\ ^\circ C$	3.5 – 4.5	0.031 – 0.037
	$T_{cell} = 60\ ^\circ C$	2 – 2.6	0.056 – 0.067
	$T_{cell} = 70\ ^\circ C$	1.2 – 1.5	0.1 -0.123
$RH_{in,c} = 0.5$	$T_{cell} = 40\ ^\circ C$	6.2 – 7.8	0.035 – 0.041
$Sto_H = 1.5$	$T_{cell} = 50\ ^\circ C$	3.44 – 4.3	0.063 – 0.073
	$T_{cell} = 60\ ^\circ C$	1.88 – 2.42	0.111 – 0.132
	$T_{cell} = 70\ ^\circ C$	1.1 – 1.4	0.144 – 0.19

7.3.2 Relationship between optimal cell operating temperature for stable operation and stoichiometric number of air

Fig.7-6 shows the relationship between the optimal cell operating temperature for stable operation and air stoichiometric number when $f = 0$. It can be seen that the ideal cell operating temperature is significantly dependent on the air stoichiometric number in this case. A high ideal cell operating temperature for stable operation requires a low air stoichiometric number. The optimal operating temperature is between 50 and 60 $^\circ C$ when considering the effectiveness of air utilization.

Fig.7-7 shows the relationship between the cell operating temperature for stable operation without external humidification and air stoichiometric number when $f > 0$. In Fig.7-7(a) and (b), the horizontal contour lines represent the constant water saturation line on the cathode side at different temperature based on Eq.7-17, and the vertical contour lines represent the constant water saturation line on the anode side at different temperature based on Eq.7-18. The curve which traces the points of intersection of the horizontal and vertical water saturation lines at the each temperature on the both cathode and the anode represents the ideal cell operating temperature line. It can be seen that the ideal cell operating temperature is increased

with decreasing air stoichiometric number and increasing f value. When increasing H_2 stoichiometric number Sto_H , the shift of ideal cell operating temperature line towards the enhanced f value is observed. In consideration of the practical air stoichiometric number for running a fuel cell, the optimal cell operating temperature range should fall within 50 to 60 °C for both $Sto_H = 1.25$ (with $f = 0.033 - 0.055$) and $Sto_H = 1.5$ (with $f = 0.065 - 0.111$), which are similar to that when $f = 0$.

Fig. 7- 6 Relationship between the ideal temperature for the stable operation and stoichiometric number of air when $f = 0$.

(a)

(b)

Fig. 7- 7 Relationship between the optimal temperature for the stable operation and stoichiometric number of air / f value, (a) $Sto_H = 1.25$ and (b) $Sto_H = 1.5$

7.3.3 Relationship between the membrane conductivity and relative humidity of water vapor of exit air

Fig.7-8 shows the relationship between conductivity of membrane and relative humidity of water vapor in the exit air. The results shows that the membrane conductivities within the relative humidity range of 0.8 and 1 are above 0.03 Scm^{-1} and temperature range of $30 - 70^\circ\text{C}$. It means that using Nafion112 (0.005 cm in thickness) at the conductivity of 0.03 Scm^{-1} will contribute $0.167 \Omega\text{cm}^2$ of the specific area resistance to the cell's total resistance. For Nafion1135 (0.0089 cm in thickness) and Nafion117 (0.0175 cm in thickness) the specific area resistances are $0.297 \Omega\text{cm}^2$ and $0.583 \Omega\text{cm}^2$, respectively. Thus, using a thin membrane would contribute a reasonably low membrane resistance to the cell resistance. On the other hand, using a thin membrane like Nafion112 would enhance the f value for improved membrane hydration.

Fig. 7- 8 Relationship between conductivity of membrane and relative humidity of water vapor of exit air

7.3.4 Relationship between the membrane conductivity and air stoichiometric number

As mentioned above, the membrane conductivity is significantly dependent on the relative humidity in a fuel cell. Thus, the membrane conductivity will be also dependent on fuel cell operating parameters such as air stoichiometric number, cell temperature, and f value which is related with membrane property. Fig.7-9 shows the relationship between the conductivity of membrane and stoichiometric number of the air at different cell temperature obtained from combining Eq.7-19 with Eq.7-20 associated with Eq.7-16 (assuming that the membrane conductivity is mainly dependent on the relative humidity of exit air). In Fig.7-9, the curve joining the circled points represents the conductivity of membrane saturated with water vapor at each respective temperature. The results in Fig.7-9 show that the conductivity of membrane is greatly dependent on the air stoichiometric number. The lower the air stoichiometric number, the higher the membrane conductivity will be. With increasing f value, the points of conductivity of membrane saturated with water vapor at each respective temperature shift towards the reduced air stoichiometric number. It can be found that the f value has more impact on the membrane conductivity at lower cell temperature as seen in Fig.7-9 (a) to (e). It is also seen that the membrane saturated with water vapor would yield proton conductivity as high as 0.112 Scm^{-1} at the temperature of 70°C with an air stoichiometric number of 1.25. However, the air stoichiometric number, as low as 1.25, would cause a large cell voltage drop due to the gas diffusion limitation polarization.

Fig. 7- 9 Relationship between conductivity of membrane and air stoichiometric number at different temperature with (a) $f = 0$, (b) $f = 0.02$, (c) $f = 0.04$, (d) $f = 0.06$ and (e) $f = 0.08$

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8.1. Introduction

Ionomer material (e.g. perfluorinated polymer) as the proton passageway extending the proton exchange membrane to active sites of the electrode can create the three-phase interface zone in the electrode active layer for electrochemical reaction. The conductivity of the perfluorinated polymer material such as Nafion is strongly dependent on the level of hydration. The water management in the active layer is also important since the Nafion material in the active layer is similar to Nafion membrane [Mosdale et al., 1995; Chan et al., 2005]. It is noted that insufficient water in the ionomer material in the active layer of electrode would increase the polarization of the electrode.

In this study, a novel method for self-humidification of fuel cells based on the internal water management is proposed. A method for humidifying Nafion material in the catalyst layer of electrode for PEMFC is presented. A self-humidifying electrode has been developed and tested without external humidification. A Nafion-silica solution containing highly dispersed nano-sized SiO₂ particles was prepared for making the self-humidifying electrode which is a conventional hydrophobic electrode. The morphology of SiO₂ particles in Nafion solution was characterized by TEM to analyze the effect of SiO₂ for self-humidifying fuel cell operation. The effects of the silica content in the self-humidifying anode on the fuel cell performance were investigated to further understand the water management in a fuel cell. The fuel cells with self-humidifying anode and different the thickness of Nafion membrane and using self-humidifying electrode for both anode and cathode were also studied.

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8.2. A new self-humidifying mechanism

A new concept for self-humidifying design is schematically shown in Fig.8-1. The MEA consists of an anode with doped nano-scale hygroscopic oxide (silica), a cathode either with or without doped nano-scale hygroscopic oxide and a Nafion membrane located between them. The nano silica particles covered with a Nafion polymer layer can serve the function of the proton transport from the Pt active site of anode into the Nafion membrane and from the membrane to the Pt active site of the cathode. In this case, the nano silica particles also play a role of water absorption. When the water produced by electrochemical reaction at the cathode back-diffuses from the cathode to the anode, it was expected to be absorbed by the silica that has a hygroscopic property. The water back-diffusion process is also help in hydrating the membrane. Since the absorption between silica and water molecular could form a strong bond by Van der Waals force, the water adsorbed by silica could not be desorbed even at the elevated temperature. Thus, silica-Nafion composite associated with water could form proton transport vehicle and conduct the protons by Grotthus mechanism (the protons are transferred from one vehicle to the other by hydrogen bonds) [Hoogers, 2003]. The silica at the cathode could help to retain water when using dry air as reactant.

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Fig. 8- 1 The schematic of a new self-humidifying concept design

8.3. Experimental

8.3.1 MEA Preparation

An in-house made carbon powder-filled gas diffusion layer consisting of PE-704 carbon paper (SGL, SIGRATHERM[®]) filled with the mixture of Vulcan XC-72R carbon powder (Cabot Co.) and PTFE (60 wt. %, Aldrich) was chosen as the electrode backing. The mass ratio of carbon to PTFE in the carbon paper was 2:1. The carbon loading in the carbon paper was 6 mg cm^{-2} . The catalyst layer, which contains the E-TEK 20 wt.% Pt/C catalyst and 60% PTFE emulsion, was formed by painting method. The Pt loading on the catalyst layer was 0.4 mg cm^{-2} for both anode and cathode. The PTFE content in the catalyst layer was 20% (based on the catalyst mass). When preparing for the catalyst layer, a homogeneous suspension of the catalyst with PTFE emulsion in isopropanol was made by mixing and stirring the mixture in an ultrasonic bath at room temperature for 0.5 hr and then kept at a low temperature for 1 hr. The suspension was then applied onto an electrode backing to form the catalyst layer. The layer was air-dried at room temperature for 1 hr, followed by a heat

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treatment at 240°C for 0.5 hr under the flowing of inert gas to remove the dispersion agent contained in the PTFE emulsion and finally sintered at 340°C for 0.5 hr.

To control a correct composition without introducing impurities, the silica powder was used in the preparation of the Nafion-silica suspension in this experiment instead of using *in situ* method (i.e., the nano-sized silica particles directly form in the Nafion solution) [Deng et al., 1998; Miyake et al., 2001; and Adjemian et al., 2002]. The home-made nano-sized silica powder was first prepared by hydrolysis/condensation reaction from Tetraethoxysilane (TEOS), deionized H₂O and HCl solution at the room temperature followed by drying the product in vacuum oven at 105 °C. The sample as prepared was then dispersed in the Nafion solution which was prepared by diluting 5% Nafion solution (DuPont) 3 to 5 folds with isopropanol, by mixing and stirring in an ultrasonic bath at room temperature for 1 hr to form the Nafion–silica suspension for use in the self-humidified electrode. The silica content in the Nafion solution (the ratio of silica to dried Nafion polymer) varied from 3%, to 10% for the study of the effect of silica content on the extent of self-humidification.

The main purpose of this study is to investigate the effect of the self-humidified anode on the fuel cell performance under the condition of insufficient external humidification. Thus, the diluted Nafion solution and Nafion-silica suspension were gun-sprayed onto the surface of the catalyst layers to form the protonized electrode and protonized/self-humidifying electrode, respectively. After the Nafion – silica suspension spray step, the electrodes were placed in a vacuum oven at 80°C and allowed them to dry for 1 hr. The Nafion loading was 1 mg cm⁻² for all the electrodes in the study.

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Nafion series, N1135, N112 and N101 (DuPont) were pretreated to remove surface impurities and various kinds of cations before they can be used. The procedure of membrane pretreatment is described elsewhere [Du et al., 2001]. A pair of the anode and cathode described above was then hot pressed onto both sides of the Nafion membranes for 2 min at 130 – 140°C with a pressure of 50 kg cm⁻².

8.3.2 Characterization and performance evaluation

A single cell with electrode area of 20-cm² and mesh flow field was used to evaluate fuel cell performances. Steady-state current-voltage measurements were first conducted on each sample at 60°C and 0.1 bars of hydrogen at the anode and 0.1 bar of air at the cathode under humidification condition, and then measured under not humidified conditions. The hydrogen pressure was controlled by Mini high-purity pressure regulator of Cole-Parmer (Max. output pressure of 1 bar) and the back pressure gauge (0 – 1 bar). The hydrogen pressure was controlled at 0.1 bars. The gas flow directions on both the anode and cathode are of counter-flow mode. The reactant gas flow rates were kept at the stoichiometric values of 1.15 times for H₂ and 2 times for air operating fuel cells at 1 Acm⁻². The testing was carried out using Arbin electronic load system.

The measurements of proton conductivity were carried out on Nafion-silica films with the varying silica contents from 0 to 10% sandwiched between two Pt disks by press at room temperature in the frequency range of 0.01–100 kHz. The potentiostat/galvanostat (model 273, EG&G) equipped with a lock-in amplifier (model 5210, EG&G) was used in this experiment. The films resistance was obtained by extrapolating the impedance data to the real axis on the high frequency side (the

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impedance data were corrected for the contribution of the empty and short-circuited cell).

The water uptake of Nafion-silica composite was determined by the gravimetric analysis. The detail of testing procedure can be found in Section 3.3.7.2 of Chapter 3.

The morphology of silica particles in the Nafion solution was examined by a transmission electron microscope (TEM) (JEM 2010, JEOL) at 100 kV. Samples of the silica dispersed in ethanol and Nafion / silica suspension were dried out on copper grids for direct observation.

8.4. Results and discussion

8.4.1 Characterizations of Nafion-silica nano-composite

TEM images of Nafion-silica composite — The size distribution of silica particle and the morphology of nano-silica particles dispersed in Nafion solution with different nano-scale silica weight percentage were observed by TEM and illustrated in Fig.8-2. It can be seen that the size of silica particles in ethanol is distributed within the diameters of about 20 to 30 nm (Fig.8-2a). The clear boundaries of silica particles are also observed. For the Nafion-silica suspensions, such as silica weight percentage of 3 and 6, silica particles were homogeneously dispersed and embedded in the Nafion matrix (Fig.8-2b and 8-2c). The composite particle size of the silica embedded in Nafion ranging from about 25 nm to 35 nm is a little bigger than that of pure silica in ethanol (Fig.8-2a). It is clear that the increase in diameter of the silica in Nafion solution is due to the covering of Nafion film on the surface of silica particles.

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Fig. 8- 2 TEM micrographs of the size distribution and morphology of Nafion and silica particles. (a) silica in ethanol, (b) 3% of silica content in Nafion, (c) 6% of silica content in Nafion and (d) 10% of silica content in Nafion.

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However, with higher percentage of silica (i.e., 10%) the network structure of the sample is formed and shows some agglomerations in various locations (Fig.8-2d). It would contribute to a poor distribution of the Nafion-silica nano-composite in the catalyst layer for electrode protonization, causing the reduction of electrode performance. In summary, the silica in Nafion-silica suspension could form Nafion-silica nano-composite particle as observed in the TEM images. This would be much beneficial to achieve a wetting effect on the Nafion covering the surface of silica particles when they are applied to the anode under operating condition.

Water uptake of Nafion-silica composite — The water uptake of Nafion-silica composite as a function of silica content is shown in Fig.8-3. The water content of the Nafion-silica composite layers increases from 0.43 to 0.79 with increasing the silica content in the measured range of 0 to 10%. The values (43% for pure Nafion and 67% for 6% of silica content) of water absorption in this experiment are much higher than those (32% for pure Nafion and 39% for 4-5% of silica content) reported by Miyake *et al.* [2001]. The higher water absorption of the composite samples in this experiment might be attributed to the loose structure of formation of Nafion-silica composite layer by the spraying method, thus more water absorption was obtained.

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Fig. 8- 3 Water content as function of silica content in Nafion-silica composite

Proton conductivity of Nafion-silica composite — The conductivity of Nafion-silica composite films under the different testing environments is reported in Table8-1. From the table, it can be seen that the conductivities of Nafion-silica composite films are dependent on the testing environment. Under fully hydrated condition (the samples immersed in the liquid water at the room temperature), the addition of silica particles in Nafion material decreases the conductivities of Nafion-silica composite films, especially for high silica content, even if the water content in Nafion-silica composite film increases with increasing in the silica content. These results appear to be in conflict with the Grotthus mechanism – transport of proton by a hopping mechanism contributes more to conduction at high water content. This can be explained by the introduction of silica particles in the Nafion material which might form a loose structure of Nafion-silica composite. Moreover, the agglomeration of silica in high content, as shown in the TEM micrograph in Fig.8-2d, may destruct the formation of continuous Nafion layer over the silica particles causing the proton conductivity to decrease further. On the contrary, at room temperature and RH of

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75%, Nafion-silica composite films have higher conductivities than that of Nafion film and show increased conductivities with the increase of the silica content from 0% to 6%, but decreased conductivity when further increase in silica content. This can be explained that the silica as hygroscopic agent would absorb the moisture from the surroundings and release the water to wet the Nafion film which covers the silica particles to improve the Nafion film conductivity. This phenomenon obeys the Grotthuss mechanism of proton transport, as mentioned above. The decrease in the conductivity at the high silica content might result from the same reason as that under fully hydrated condition described above.

Table 8- 1 Proton conductivity (Scm^{-1}) measured on Nafion and Nafion-silica composite films

Testing condition	0 wt% of SiO_2	3 wt% of SiO_2	6 wt% of SiO_2	10 wt% of SiO_2
In the water at the room temperature	0.0207	0.0177	0.0164	0.013
In RH of 75% at the room temperature	0.0083	0.0101	0.012	0.0097

8.4.2 Performance of PEMFCs with various silica contents in anodes under humidified and dry reactant gas conditions

Fig.8-4 shows the current-voltage characteristics of single cells using Nafion112 as the electrolyte and self-humidifying anodes with various silica contents in Nafion–silica composite operated on either humidified or non-humidified gases. Under the externally humidifying condition at 65/60/60°C ($T_{\text{anode humidifier}}/T_{\text{cell}}/T_{\text{cathode humidifier}}$), the cells with 0%, 3% and 6% of silica in anode exhibit similar cell performance over the whole current density range, *i.e.*, cell voltage of 0.7 V at about 450 mA cm^{-2} and the maximum power density of about 0.47 W cm^{-2} . However, the cell with 10% of silica in anode shows the poorest performance, *i.e.*, cell voltage of 0.65 V at about 450 mA cm^{-2} and the maximum power density of about 0.41 W cm^{-2} (Fig.8-4a). The results

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indicate that the silica content has little effect on the anode and hence the cell performance when the quantity is low and humidity is high. It is revealed that the Nafion-silica nano-composites, as clearly observed in the TEM image (Fig.8-2c), function like the proton conductor similar to the Nafion material in the catalyst layer and provide the passageways for proton transport from the catalyst sites to the membrane. However, with high percentage of silica in the anode, *i.e.*, 10%, the performance of the cell is impaired likely due to the agglomerations of silica particles in the catalyst layer, thus causing reduced proton conductivity of Nafion-silica nano-composite. This is supported by the evidence of the result in Table 8-1.

(a)

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(b)

Fig. 8- 4 Performances of single cells using self-humidifying anode with various silica contents measured at 60 °C (a) under the externally humidified condition of 65/60/60 ($T_{\text{anode humidifier}}/T_{\text{cell}}/T_{\text{cathode humidifier}}$), (b) without any external humidification

Fig.8-4b shows the performances of cells with self-humidifying anodes operating at cell temperature of 60°C without external humidification. It is found that the performances of the cells increase with the increase in the silica to Nafion ratio in anodes from 0 up to 6%, *i.e.*, the cell voltage increases from 0.56 to 0.66 V at about 450 mAcm⁻² and the maximum power density enhances from 0.26 to 0.4 Wcm⁻². However, further increase in silica to 10% causes deteriorated performance as illustrated by the decreased cell voltage from 0.66 to 0.61 V at the same current density and the decreased maximum power density from 0.4 to 0.35 Wcm⁻². In contrast, the cell without silica in the anode shows the poorest fuel cell performance. This explicitly indicates that adding silica in the anode catalyst layer could improve the performance of fuel cell under non-humidified condition. It can be explained that the addition of silica in the anode catalyst layer would improve the water uptake of the Nafion material in the anode catalyst layer so that the proton conductivity could

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be increased under a low humidity. This is in good agreement with the results on the characterizations of water uptake and proton conductivity for Nafion-silica composite as described in Section 8.4.2. It can provide evidence that the Nafion-silica composite in the active layer (of anode) would hold more water than the pure Nafion material under the non-humidification condition. The water absorbed in the Nafion-silica composite mainly comes from the water back-diffusion through the membrane from the cathode to the anode (some water may be formed from the recombination of permeated oxygen and hydrogen at the anode). The membrane would simultaneously be self-humidified by the water transported through it due to the back-diffusion. Thus, not only could the over-potential of anode but the membrane resistance be reduced by adding silica into the Nafion material in the anode for increasing the cell performance at the non-humidification condition. On the other hand, the added silica as a hygroscopic agent would help in retaining the water especially when considerable back diffusion of water from the cathode to the anode occurs under no/low load operations. This effect is particularly profound when ultra thin membrane is used because of reduced number of water molecules per proton drag and the large concentration gradient of water across the ultra thin membrane. The silica content and its distribution in the catalyst layer also play an important role in the improvement of fuel cell performance. Though, the increase in the silica content in the catalyst layer allows higher chances for Nafion to come in contact with silica particles and arrives in good distribution throughout the electrode for increased catalyst utilization, high silica content like 10% tends to form agglomerates that would block the passageway of proton conduction in the catalyst layer, and thus hinder the performance of the fuel cell. In addition, in the high current density region, the voltages of the cells drop faster under the case without external humidification with increasing in the current

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density, especially for electrodes without silica (see Fig.8-4b). This might be caused by the water imbalance in the cells due to the high water electro-osmotic drag at high current density. In general, the self-humidifying anode with enhancing silica content can improve the performance of the fuel cell under no external humidifying condition, but the performance of the cells is poorer compared to those under proper external humidification. For example, the maximum power outputs reduce 44%, 25%, 11% and 12% for the self-humidifying anodes added with silica contents of 0%, 3%, 6% and 10 %, respectively, compared with the one with proper external humidification. It indicates that the membrane and Nafion material in the catalyst layer under no external humidification may not be fully hydrated.

8.4.3 Stability test

A fuel cell stability test was conducted using the self-humidifying anode added with silica contents of 6% (in comparison with an anode without adding silica) at the cell temperature of 60°C / 50 °C under non-humidifying condition for both H₂ and air feedstock (Fig.8-5). The fuel cells were operated at a constant current density of 600 mAcm⁻² and the cell voltage changes were recorded. Before the stability testing, the fuel cells were conducted under humidifying condition at 65°C/60°C/60°C ($T_{\text{anode humidifier}}/T_{\text{cell}}/T_{\text{cathode humidifier}}$) for about 1 hr to achieve a stable fuel cell performance. Then, the stability testing was carried out under the non-humidifying condition at the cell temperature of 60 °C followed by tested at the cell temperature of 50°C. The reactant gas flow rates were kept at the stoichiometric values of 1.15 times for H₂ and 2 times for air operating fuel cells at 1 Acm⁻². The fuel cell with the self-humidifying anode demonstrates much higher stable voltage at a constant current density than that of the fuel cell with a normal anode. The fuel cell with the self-humidifying anode also shows a higher voltage at 60°C than that at 50°C, while the cell with a normal

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anode displays a higher voltage at 50⁰C than that at 60⁰C. It indicates that the fuel cell with the self-humidifying anode has achieved a significant self-humidifying effect. For the cell with a normal anode, the enhanced voltage at 50⁰C is due to the lower water vapor saturation pressure in the cell at 50⁰C than that at 60⁰C, so that the water loss in the membrane at 50⁰C would be alleviated. From the macro-model developed in Chapter 7, we have known that stability operation of a normal PEM fuel cell with self-humidification is highly dependent on the operating temperature, stoichiometric values of both H₂ and air, and f value (the net water flow rate through the membrane from the cathode to the anode). Based on this model, we can estimate the optimal temperature for stable operation is about 42 °C at the operating conditions for this stability tests ($p_{H_2} / p_{air} : 0.1 / 0.1$ bar; stoichiometric value for H₂ 1.92 and for air 3.33 at the current density of 600 mAcm⁻²; assuming f value 0.09). An increase in the cell temperature above the optimal temperature lowers the relative humidity at the both anode and cathode chambers and decreases the conductivity of electrolyte membrane, thus the fuel cell performance decreases. In summary, the fuel cell with a self-humidifying anode has much higher stability at the enhanced cell temperature than the fuel cell with a normal anode. It further proves that the anode added with Nafion/silica can serve the self-humidifying function.

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Fig. 8- 5 The stability testing of the fuel cell with a self-humidifying anode compared to the fuel cell with a normal anode

8.4.4 Effect of thickness of membrane

Fig.8-6 shows the effect of the thickness of Nafion membranes (25 μm for N101, 50 μm for N112, and 89 μm for N1135) on the fuel cell performance using the same self-humidifying anodes with the silica content of 6%. It is found that the thickness of the membrane has more impact on the performance of the cells in the case without external humidification (see symbol curve) than that with external humidification at 65/60/60°C (line curve). The improvement is due to the combined effect of the reduced proton conduction length and the increased conductivity due to considerable back diffusion of water particularly favorable to ultra thin membrane, as mentioned in Section 3.2. At the high current density, the increased electro-osmotic drag causes a steep rise of the internal resistance of the cell due to the water imbalance in the membrane under no external humidification condition, thus causing the cell voltage to drop abruptly besides the mass transport limitation. The effect on the cell performance is increasingly serious with increase in the thickness of the membrane.

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Fig. 8- 6 Performances of single cells using self-humidifying anode (containing 6% of silica) with various thickness of Nafion membranes (N1135 with 89 μ m, N112 with 50 μ m and N101 with 25 μ m) measured at 60 °C.

8.4.5 Performance of PEMFCs with self-humidifying electrode on the both anode and cathode under dry reactant gas conditions

Fig.8-7 shows the performance of the fuel cell with the self-humidifying electrode (with 6% silica) for both anode and cathode under dry reactant gas condition in comparison with the fuel cells with self-humidifying anode only under the humidifying condition (65/60/60°C) and non-humidifying condition at 60°C. It can be seen that the addition of nano-silica particles at the cathode can significantly improve the oxygen transport at the cathode in the fuel cell under dry reactant condition. The fuel cell with the self-humidifying electrode for both anode and cathode under dry reactant condition can provide a larger limiting current than the normal cathode in the fuel cell under the external humidifying condition. It is believed that the nano-silica combined with Nafion polymer at cathode would have served two functions (1) retaining water produced at the cathode and (2) enhancing the oxygen diffusion in the catalyst layer. However, the introduction of silica particles into the cathode may not

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be helpful to the fuel cell operating under the humidifying condition due to possible cathode flooding to be occurred. It was proved by Jung et al. [2005].

Fig. 8- 7 The performance of the fuel cell with the self-humidifying electrode (adding 6% silica) for both anode and cathode under dry reactant gas condition in comparison with the fuel cells with self-humidifying anode only under the humidifying condition (65/60/60°C) and non humidifying condition at 60°C under 0.1 bar for both H₂ and air

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In this study, a new type of gas diffusion layer - a carbon-filled gas diffusion layer (CFGDL) and a novel self-humidifying electrode – silica added electrode have been developed for PEMFC performance improvement. The performance and microstructure of the membrane electrode assembly related to CFGDL and the self-humidifying electrode – silica added electrode were investigated by various experimentations associated with model analysis. From these studies the following conclusions can be drawn.

9.1 Effect of the structure of gas diffusion layer

A comparative study of electrodes with conventional one-layer GDL, dual-layer GDL and carbon-filled GDL was carried out systematically. The properties of electrodes were characterized by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), field-emission scanning electron microscope (FESEM), transmission electron microscope (TEM), mercury intrusion porosimetry (MIP), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and steady-state polarization gain insights into the relationships between electrochemical behavior of electrode / cell performance and GDL structure. For instance, the results from SEM and EDS indicate that CFGDL and dual-layer GDL have a good support for Pt/C catalyst particles if the catalyst is directly deposited on their surface. It is consistent with the high Pt utilization of CFGDL and dual-layer GDL from CV measurement. The results from SEM also show that CFGDL has the same thickness of 0.11 mm as that of one-layer GDL, while dual-layer GDL has the thickness of 0.18 mm. This indicates that the mass transport through one-layer GDL and CFGDL should have the same distance for diffusion from the flow field to the catalyst layer or

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from the catalyst layer to the flow field, while the mass transport through the dual-layer GDL has a long-distance diffusion path. On the other hand, the results from MIP showed that CFGDL has a porosity of 67 % with approximately 4.7 μm average diameter pores; one-layer GDL has a porosity of 77% with approximately 35.8 μm ; and dual-layer GDL has a porosity of 73% with approximately 25.5 μm diameter pores. In principle, one-layer GDL should have the best mass transport property due to the highest porosity and CFGDL would have the poorest mass transport property due to the lowest porosity. However, the results from EIS show that CFGDL has the best electrochemical reaction performance and a good mass transport property. It has been verified by the steady-state polarization measurement and fuel cell kinetics analysis. The good electrochemical reaction performance of CFGDL originates from the high Pt utilization due to a good support of CFGDL for Pt/C catalyst. The good mass transport property of CFGDL is attributed to the appropriate microstructure of CFGDL. As reported by Wilson et al. [1995], the greater the pore size of an electrode backing (GDL), the poorer the performance will be. It was suggested that serious flooding occurs in the large pore structures, most noticeably on the cathode side. The results from the bulk resistance measurement show that CFGDL has the smallest electrical resistance and one-layer GDL has a smaller electrical resistance than that of dual-layer GDL. In summary, the GDL performance is closely related to the structural design and microstructure of GDL. It is found that CFGDL has the optimal physical structure and microstructure based on the experimental results.

9.2 Optimization of the composition of CFGDL

Based on the proposed concept of two parallel conducting networks, macro-porous substrate (carbon paper) and conductive filler (carbon and PTFE mixture), in the CFGDL electrical system, a model establishing the relationship between the

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resistivity and carbon loading of CFGDL has been developed. Good agreement between the experimental result and the fitted result by the model was observed. From the conductivity measurements and theoretical analysis, it is found that the carbon content of 6 mg cm^{-2} and 40% PTFE are the optimum compositions for CFGDL to achieve the best electrical property.

The loading of the carbon in the CFGDL significantly affects the performance of the fuel cell in all three polarization regions, i.e., activation (mainly at the cathode), mass transport, and ohmic controlled. The poor support of CFGDL for catalyst layer at lower carbon loading will cause the loss of Pt loading in catalyst layer and thus increases the activation overpotential. Increasing the carbon loading in the CFGDL can reduce the internal resistance of the cell and hence improves the fuel cell performance mainly due to the decrease in the contact resistances between the interfaces of both GDL/catalyst layer (CL) and CL/electrolyte membrane. Increasing the carbon loading in CFGDL can also reduce the mass transport limitation due to the improvement of water management as reported by Wilson et al. [1995]. However, excessive carbon loading in CFGDL decreases the porosity and thus increases the concentration overpotential, in particular for the H_2 /air fed fuel cell, which is due to decreased gas diffusion coefficient in the CFGDL. Unlike the effect of carbon loading, the PTFE content of the CFGDL at the optimal carbon loading affects on the polarization performance of the cell only in the ohmic and mass transport control polarization regions. It is believed that the major contribution of PTFE in CFGDL on the ohmic polarization is from the electrical contact resistance between the interface of CFGDL and CL. The mass transport polarization caused by PTFE content comes from the resistance of gas diffusion due to the changed porosity in CFGDL and water flooding due to the changed hydrophobicity of CFGDL.

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The significant effect of the carbon loading in CFGDL on the utilization of Pt is confirmed in the study. With fixed PTFE content of 40%, increasing the carbon loading from 2 to 8 mg cm⁻² in CFGDL increased the Pt utilization from 16% to 52%. This might be attributed to the reduction of the surface cracks, thus providing better support for the Pt catalysts. A rather insignificant effect of PTFE content on the utilization of Pt was found, except for excessively high PTFE content of 60%.

Furthermore, the carbon loading at a fixed PTFE content and PTFE content at a fixed carbon loading significantly change the micro-structure of the CFGDL. The local porosity in the ordinary (molecular diffusion) controlled regime (1 – 20 μm) is the main contribution to the total porosity of CFGDL. It is believed that the optimal composition of CFGDL should be the carbon loading between 4 – 6 mgcm⁻² and PTFE content of 30 - 40% based on the analysis of pore size distribution in the study.

Finally, the best performance of the PEMFC has been achieved when using PE-704 carbon paper (SGL, SIGRATHERM[®] paper) filled with 6 mg cm⁻² of carbon and 40% PTFE.

9.3 Effect of PTFE content in CFGDL on the mass transport

The important parameters for evaluating the two-phase flow and transport – water saturation, liquid volume fraction and gas volume fraction of CFGDL were obtained experimentally based on the proposed water uptake measurement and porosity characterization. These parameters are significantly affected by the PTFE contents.

The wetting property of CFGDL was evaluated by the modified Wilhelmy method. The measured contact angles of CFGDL in the low PTFE content range are significantly dependent on the PTFE content. The measured contact angles of CFGDL have maintained a constant value between the PTFE content of 40% and

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60%. The threshold value is 40% of PTFE in CFGDL. It has been found that the intrinsic contact angles of CFGDLs, which were obtained from correcting the measured contact angle using the Cassie-Baxter equation, is less than the measured contact angle. For instance, the CFGDL with PTFE content of 10% has an intrinsic contact angle of 83° compared to the measured contact angle of 108° . This indicates that the CFGDL with PTFE content of 10% has presented an intrinsic hydrophilic surface.

The effect of flooding on oxygen transport and fuel cell performance under the both H_2/O_2 and H_2/air operating conditions was analyzed using a model developed for flooding. Significant increase in the cathode overpotential is predicted with increased liquid saturation (level of flooding), particularly at high current densities. It is found that the cathode overpotential is significantly dependent on the PTFE content in GDL and decrease in the PTFE content in GDL results in an increase in cathode overpotential at the same mobile liquid saturation. This is attributed to the effect of the immobile liquid saturation in GDL, since decrease in the PTFE content in GDL results in an increase in the immobile liquid saturation in GDL. The loss due to mass diffusion limitation in the electrode is seriously controlled by the water saturation of GDL at high current density. For instance, the appearance of mass transport limitation with the PTFE content of 10% in GDL at high current density, when using pure H_2 and O_2 as reactants, is attributed to the high immobile saturation to be relevant to a small intrinsic contact angle of such a GDL. In summary, the analysis by the developed model, in which the water saturation is incorporated, shows that the mass transport limitation of fuel cells at high current density is attributed to the water flooding when using CFGDL with a lower PTFE content. It is in good agreement with the steady-state polarization measurement.

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9.4 A new macro-model for predicting the possibility of the self-humidifying operation

A new macro model for predicting the possibility of the self-humidifying operation in PEMFC under nearly ambient H_2 /air pressures without external humidification was developed. From the theoretical analysis, some important findings are: (1) the self-humidifying operation of PEMFC is highly dependent on the cell operating temperature, air stoichiometric number and net water back-diffusion from the cathode to the anode; and is little dependent on the relative humidity of inlet air (at the ambient condition (25 °C)) (2) Under H_2 “dead end” operation, the stable cell operation with the self-humidification can be achieved at temperature from 30 °C to 70 °C without consideration of reasonable air stoichiometric number and net water back-diffusion (f value); the optimal cell operating temperature for stable cell operation is 60 °C with $Sto_c = 2$ (the effective air usage) (3) Under H_2 non “dead end” design, the stable cell operation with the self-humidification can be also achieved at the temperature from 30 °C to 70 °C without consideration of reasonable air stoichiometric number and net water back-diffusion (f value); in this case, the hydrogen stoichiometric number will affect the stable cell operation; the optimal cell operation temperature for stable cell operation is similar to that under H_2 “dead end” operation with $Sto_c = 2$ (the effective air usage). In general, the use of thin electrolyte membrane with introduction of hygroscopic agent into the membrane (enhancing water diffusion coefficient) or adding hygroscopic agent at anode catalyst layer is beneficial to the water back-diffusion, i.e. to increase f value, the cell self-humidifying operation under a high temperature could be achieved.

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9.5 A novel self-humidifying membrane electrode assembly (MEA)

Self-humidification was achieved by using a conventional hydrophobic electrode protonized by the Nafion – silica suspension. The results from TEM images showed that the nano-sized silica particles were uniformly dispersed and embedded in the Nafion matrix to form the Nafion-silica nano-composite which functions like the proton conductor as Nafion material in the catalyst layer of the electrode. However, the network structure and some agglomerates of silica particles were observed with the high percentage (i.e., 10%) of silica dosage. The addition of silica in the Nafion matrix could improve the water absorption of the Nafion material from the evidence of water uptake measurement. The water content of the Nafion-silica composite layers increases with increasing the silica content in the measured range. The Nafion-silica composite films exhibit a little lower conductivity than that of Nafion film under the fully hydrated condition. On the contrary, the addition of silica in the Nafion matrix could improve the proton conductivity of the Nafion material at the ambient condition with RH of 75% and room temperature. An optimal catalyst layer formed by Nafion-silica nano-composite in the catalyst layer was found to be with 6 % of silica content. When the silica used is more than necessary, *i.e.*, 10%, undesirable fuel cell performance occurs which would be attributed to the formation of agglomerations of silica particles in the Nafion-silica composite structure shown in the TEM image. The results obtained from a single cell operation showed that the anodes sprayed with Nafion - silica suspension have significant improvement on the cell performance under no external humidification condition compared with the anode sprayed with pure Nafion solution. It was attributed to the fact that the presence of the silica as a hygroscopic agent in the anodes retains the water due to the considerable back diffusion of water molecules from the cathode to the anode or the possible

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recombination of permeated oxygen and hydrogen at the anode to hydrate the Nafion in the catalyst layer for effective proton conduction. Improved performance of single cells using thinner membrane with silica-added anode was obtained under no external humidification condition due to more effective back-diffusion of water molecules in thinner membrane. The fuel cell with silica-added anode has much better stability at elevated cell temperature than the fuel cell with a normal anode. It further proves that the anode added with Nafion-silica performs the self-humidifying function for PEM fuel cell. The addition of nano-silica particles at the cathode can significantly improve the oxygen transport at the cathode in the fuel cell under dry reactant condition.

9.6 Recommendation for further studies

The following subjects are suggested for further development:

- (1) The effects of carbon loading and PTFE content in CFGDL on the microstructure and performance of CFGDL were studied with various physical analysis techniques and electrochemical characterizations. The experimental results showed that the carbon loading in the CFGDL plays a critical role in the properties of CFGDL. However, carbon materials with different surface area would also affect their electrode performance associated with morphological characteristics of GDL. Thus, the investigation of the effects of carbon materials with different surface area on the microstructure and performance of CFGDL is suggested.
- (2) The addition of nano-silica particles at the cathode can significantly improve the oxygen transport (increase the limiting current) at the cathode in the fuel cell. The mechanism of increasing oxygen transport and kinetics of oxygen reduction in the Nafion polymer with the addition of nano-silica particles should be understood.

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The approach using a rotating Pt disk electrode filmed with a thin film of Nafion/silica to evaluate the concentration and diffusion coefficient of oxygen in the film of Nafion/silica is suggested.

- (3) In this study of self-humidifying design, a hydrophobic electrode (catalyst layer containing PTFE) was chosen and protonized by Nafion-silica material instead of Nafion material. In consideration of the preparation of thin-film electrode or catalyst coated membrane (CCM), it is suggested that Nafion-silica material be directly added into catalyst when preparing catalyst layer for the further study of the self-humidifying mechanism.
- (4) Based on the new concept of self-humidifying design in this thesis, it is suggested that further studies on this self-humidifying mechanism with other hygroscopic materials, such as TiO_2 , ZrO_2 etc., be carried out. A study on the combination of a self-humidifying electrode with self-humidifying membrane developed by Watanabe et al. [1996] is also suggested.

LIST OF PUBLICATIONS

List of Publications

During This Ph.D. Candidature

I. Internationally Referred Journals

1. “Development of carbon-filled gas diffusion layer for PEFCs”, M. Han, S.H.Chan, and S.P. Jiang, *Journal of Power Sources*, 159 (2006): 1005-1014
2. “Investigation of Self-humidifying Anode in Polymer Electrolyte Fuel Cells”, M. Han, S.H.Chan, and S.P. Jiang, *International Journal of Hydrogen Energy*, 32 (2006): 385-391
3. S.H. Chan, M. Han and S.P. Jiang, “Guidelines for stable operation of a polymer electrolyte fuel cell with self-humidifying membrane electrolyte assembly”, *Journal of the Electrochemical Society*, 154 (2007): 486-493
4. M. Han, S.H. Chan and S.P. Jiang, “Gas Diffusion Layers in PEFC – A Full Characterization”, submitted to *Electrochimica Acta*
5. M. Han, S.H. Chan and S.P. Jiang, “Analysis of water flooding in gas diffusion layer for PEM fuel cells”, in preparation
6. M. Han, S.H. Chan and S.P. Jiang, “Effect of PTFE content on the mass transport in gas diffusion layer for PEMFCs”, in preparation

II. Papers Presented at Conferences

1. “Investigation of Self-humidifying Membrane Electrode Assembly in PEM Fuel Cells”, M. Han, S.H. Chan and S.P. Jiang, The 3rd Guangzhou Fuel Cell Conference 20 – 23 June, 2006, Guangzhou, China
2. “The effect of PTFE content on the properties of carbon-filled gas diffusion layer for polymer electrolyte fuel cells”, M. Han, S.H. Chan and S.P. Jiang, The 5th International Conference on Materials Processing for Properties and Performance (MP3), 11 - 15 December 2006, Singapore

III. Patent

1. “Self Hydrating membrane electrode assemblies for fuel cells” Application of US Patent (2006.9, Application No. 60/824,874), pending

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APPENDIX 1

Appendix 1

I. Calculation of the oxygen pressure at the gas diffusion layer/catalyst layer interface of cathode

In Fig 1, the gaseous reactant O_2 , which is usually mixed with nitrogen and water vapor (i.e., humidified air), enters the cathode gas flow field, transports through the porous gas diffusion layer, and dissolves into the membrane phase of the active catalyst layer. Assume that (1) one-dimensional diffusion in the gas diffusion layer; (2) pressure changes in the flow field and gas diffusion layer are small; (3) the entire system is taken to be held at constant temperature; and (4) the inlet gases are fully saturated with water at inlet condition.

Fig. A1-1 Schematic diagram of fuel cell model

1. Air feed

When air, i.e., a mixture of oxygen and nitrogen, is saturated with water vapour at the fuel cell operating temperature, we know the mole fractions, x , and partial pressures, p , are related to the total pressure, P_t , by

$$x_{O_2} + x_{N_2} + x_w^{sat} = 1 \quad (1)$$

APPENDIX 1

or

$$p_{O_2} + p_{N_2} + p_w = P_t \quad (2)$$

With constant pressure and temperature in the flow fields, i.e., the partial pressure of water vapour is at the saturation vapour pressure, the gas-phase flux of water normal to the cathode face is zero. As nitrogen is not removed from the diffusion channel, the net nitrogen gas-phase flux normal to the cathode face is also zero:

$$N_{w,g} = 0 \text{ and } N_{N_2,g} = 0 \quad (3)$$

Thus by combining the above equations the one-dimensional Stefan-Maxwell equation for nitrogen is

$$\frac{dx_{N_2}}{dz} = \frac{RT}{PD_{N_2-O_2}^{eff}} (x_{N_2} N_{O_2,g}) \quad (4)$$

The gas-phase flux of oxygen is given by

$$N_{O_2,g} = \frac{I}{4F} \quad (5)$$

where I is the cell current density.

Thus Eq. (4) yields the mole fraction of nitrogen at the gas diffusion layer/catalyst layer interface of cathode, $x_{N_2}^{interface}$, as

$$x_{N_2}^{interface} = x_{N_2}^{flowfield} \exp \left[\frac{RTI\delta_d}{4FP_t D_{N_2-O_2}^{eff}} \right] \quad (6)$$

where δ_d is the thickness of the gas diffusion layer, $x_{N_2}^{flowfield}$ is the mole fraction of nitrogen in the flow field, and $D_{N_2-O_2}^{eff}$ is the effective diffusivity, which can be expressed by [Belfiore, 2003]

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$$D_{N_2-O_2}^{eff} = (\varepsilon / \tau) D_{N_2-O_2} \quad (7)$$

where ε is the porosity of gas diffusion layer and τ the tortuosity.

The partial pressure of oxygen at the gas diffusion layer/catalyst layer interface can now be calculated using Eq. (2)

$$p_{O_2}^{interface} = P[1 - x_w^{sat} - x_{N_2}^{interface}] \quad (8)$$

Combining Eqs. (6), (7) and (8) gives

$$p_{O_2}^{interface} = P_t \left[1 - x_w^{sat} - x_{N_2}^{flowfield} \exp \left(\frac{RTI\delta_d}{4FP_t(\varepsilon / \tau) \cdot D_{O_2-N_2}} \right) \right] \quad (9)$$

where ε is the gas-phase void fraction (wet-proofed pores) and $D_{O_2-N_2}$ is the diffusivity of nitrogen in oxygen given by the Slattery and Bird correlation [2001, 2nd edition]

$$PD_{O_2-N_2} = a \left(\frac{T}{\sqrt{T_{O_2}^{crit} T_{N_2}^{crit}}} \right)^b (P_{O_2}^{crit} P_{N_2}^{crit})^{1/3} \times (T_{O_2}^{crit} T_{N_2}^{crit})^{5/12} \left(\frac{1}{M_{N_2}} + \frac{1}{M_{O_2}} \right)^{1/2} \quad (10)$$

With appropriate values (Table I) for the known constants, Eqs. (9) and (10) yield

$$p_{O_2}^{interface} = P \left[1 - x_w^{sat} - x_{N_2}^{flowfield} \exp \left(\frac{35I\delta_d}{(\varepsilon / \tau) T^{0.832}} \right) \right] \quad (11)$$

APPENDIX 1

Table A1-I. Critical Properties [Bird et al., 2001]

Parameters	Values
$P_{N_2}^{crit}$	33.5 atm
$P_{O_2}^{crit}$	49.7 atm
$T_{N_2}^{crit}$	126.2 K
$T_{O_2}^{crit}$	154.4 K
$P_{H_2O}^{crit}$	220.06 atm
$T_{H_2O}^{crit}$	647.1 K
M_{N_2}	28
M_{O_2}	32
M_{H_2O}	18
a for nonpolar gas pairs (N ₂ and O ₂)	2.745×10^{-4}
b for nonpolar gas pairs (N ₂ and O ₂)	1.823
a for pairs of H ₂ O and nonpolar gas	3.640×10^{-4}
b for pairs of H ₂ O and nonpolar gas	2.334

2. Oxygen feed

In the case when the cathode feed stream contains only water vapour and oxygen, Eq. (2) indicates that the drop in oxygen partial pressure along the diffusion path will result in a corresponding drop in the total pressure. There will thus be a molecular flux of water vapour “out” just sufficient to balance the bulk motion of the gas due to the diffusion of oxygen “in” and the net flux of water vapour through the cathode is zero.

In this case the Stefan-Maxwell equation leads to

$$\frac{dx_{O_2}}{dz} = \frac{RT}{PD_{H_2-O_2}} \left(x_w \frac{I}{4F} \right) \quad (12)$$

Since $x_{O_2} + x_w = 1$, integration of this expression from the flow field to the catalyst surface, assuming the product $PD_{i,j}^{eff}$ is constant, gives

APPENDIX 1

$$x_w^{interface} = x_w^{flowfield} \exp\left(\frac{RTI\delta_d}{4FPD_{H_2O-O_2}^{eff}}\right) \quad (13)$$

As the partial pressure of water vapour in the cathode is fixed at the saturation level, the partial pressure of oxygen at the interface is

$$p_{O_2}^{interface} = (1 - x_w^{interface}) \left(\frac{p_w^{sat}}{x_w^{interface}} \right) \quad (14)$$

Combining Eqs. (13) and (14) yields

$$p_{O_2}^{interface} = p_w^{sat} \left[\frac{1}{\exp\left(\frac{RTI\delta_d}{4FPD_{H_2O-O_2}^{eff}}\right) \cdot x_w^{flowfield}} - 1 \right] \quad (15)$$

Evaluation of the Slattery-Bird equation for $PD_{H_2-O_2}^{eff}$ gives

$$p_{O_2}^{interface} = p_w^{sat} \left[\frac{1}{\exp\left(\frac{503I\delta_d}{(\varepsilon/\tau)T^{1.334}}\right) \cdot x_w^{flowfield}} - 1 \right] \quad (16)$$

II. Calculation of the mean concentrations of gases in the flow field

1. Calculation of $x_{N_2}^{flowfield}$ (air feed)

The mole fraction of oxygen in the humidified inlet and outlet gas streams can be determined from the dry gas compositions and the mole fraction of saturated water vapour. It is given by

$$x_{O_2,in}^f = (1 - x_w^{sat}) \cdot x_{O_2}^{in} \quad (17)$$

$$x_{O_2,out}^f = (1 - x_w^{sat}) \cdot x_{O_2}^{out} \quad (18)$$

APPENDIX 1

where $x_{O_2,in}^f$ and $x_{O_2,out}^f$ are defined as the mole fraction of oxygen in the humidified inlet and outlet gas stream in the flow field, respectively, $x_{O_2}^{in}$ and $x_{O_2}^{out}$ are the mole fraction of oxygen in the dry inlet and outlet gas streams, respectively.

The $x_{O_2}^{out}$ can be expressed in terms of $x_{O_2}^{in}$ and the oxygen stoichiometric ratio ζ (the ratio of the inlet flow rate of oxygen to the rate at which it is consumed in the electrochemical reaction) by

$$x_{O_2}^{out} = \frac{1}{1 + \frac{\zeta}{\zeta - 1} \cdot \frac{x_{N_2}^{in}}{x_{O_2}^{in}}} \quad (19)$$

where $x_{N_2}^{in}$ is the mole fraction of nitrogen in the dry inlet gas stream.

Substitution of Eq. (19) into Eq. (18) results in

$$x_{O_2,out}^f = \frac{1 - x_w^{sat}}{1 + \frac{\zeta}{\zeta - 1} \cdot \frac{x_{N_2}^{in}}{x_{O_2}^{in}}} \cdot \quad (20)$$

As approximation, the mean mole fraction of oxygen is given by a log-mean average of the inlet and outlet mole fractions of oxygen in the flow field.

$$x_{O_2}^{flowfield} = \frac{x_{O_2,in}^f - x_{O_2,out}^f}{\ln\left(\frac{x_{O_2,in}^f}{x_{O_2,out}^f}\right)} \quad (21)$$

Substitution of Eqs. (17) and (20) into Eq. (21) results in

$$x_{O_2}^{flowfield} = \frac{(1 - x_w^{sat})(\chi \cdot x_{O_2}^{in} - 1)}{\chi \cdot \ln(\chi \cdot x_{O_2}^{in})} \quad (22)$$

where χ represents the expression

$$\chi = 1 + \frac{\zeta}{\zeta - 1} \cdot \frac{x_{N_2}^{in}}{x_{O_2}^{in}} \quad (23)$$

APPENDIX 1

From Eq. (1), the mean mole fraction of nitrogen, $x_{N_2}^{flowfield}$, in the flow field can be obtained by

$$x_{N_2}^{flowfield} = \frac{(1 - x_w^{sat})[\chi \ln(\chi \cdot x_{O_2}^{in}) - \chi \cdot x_{O_2}^{in} - 1]}{\chi \ln(\chi \cdot x_{O_2}^{in})} \quad (24)$$

2. Calculation of $x_w^{flowfield}$ (oxygen feed)

If using dry oxygen ($x_w^{in} = 0$) at the inlet and assuming the oxygen saturated with water at the outlet ($x_w^{out} = x_w^{sat}$), the mean mole fraction of water is given by an arithmetic-mean average of the inlet and outlet mole fractions of water in the flow field.

$$x_w^{flowfield} = \frac{x_w^{in} + x_w^{sat}}{2} = \frac{1}{2} x_w^{sat} \quad (22)$$

APPENDIX 2

Appendix 2

I. Saturated vapour pressure formula for Water (0 – 100°C)

Table A2-I. Saturated vapour pressure for water [Weast, 1966]

Temp. (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)
0	0.00603	34	0.0525	68	0.2818
1	0.00648	35	0.05549	69	0.29438
2	0.00697	36	0.05864	70	0.3075
3	0.00748	37	0.06193	71	0.32092
4	0.00803	38	0.06538	72	0.335
5	0.00861	39	0.069	73	0.34961
6	0.00923	40	0.07279	74	0.36474
7	0.00989	41	0.07676	75	0.38039
8	0.01059	42	0.08092	76	0.39658
9	0.01133	43	0.08526	77	0.41329
10	0.01212	44	0.08982	78	0.43066
11	0.01295	45	0.09458	79	0.44868
12	0.01384	46	0.09954	80	0.46724
13	0.01478	47	0.10474	81	0.48645
14	0.01577	48	0.11014	82	0.50645
15	0.01683	49	0.11582	83	0.52711
16	0.01794	50	0.12172	84	0.54842
17	0.01912	51	0.12789	85	0.57053
18	0.02036	52	0.13433	86	0.59329
19	0.02168	53	0.14105	87	0.61671
20	0.02307	54	0.14804	88	0.64092
21	0.02454	55	0.15532	89	0.66592
22	0.02609	56	0.16292	90	0.69179
23	0.02772	57	0.17082	91	0.71849
24	0.02944	58	0.17905	92	0.74604
25	0.03126	59	0.18763	93	0.77447
26	0.03317	60	0.19655	94	0.80382
27	0.03518	61	0.20583	95	0.83408
28	0.0373	62	0.21549	96	0.86529
29	0.03953	63	0.2255	97	0.89746
30	0.04187	64	0.23593	98	0.93062
31	0.04434	65	0.24676	99	0.96479
32	0.04692	66	0.25801	100	1
33	0.04964	67	0.26968		

APPENDIX 2

Fig.A2-1. Relationship between vapour saturated pressure and temperature for water

The formula of vapour saturated pressure for water can developed based on Fig.A2-1 and expressed by,

$$p_T^{sat} = -0.03089 + 0.02451 \exp\left(\frac{T}{26.6731}\right) \quad (25)$$

and the unit of the p_T^{sat} is atm, and the unit of the temperature T is °C.