

CHAPTER II LITERATURE REVIEW

2.1 Basic Principle of Fuel Cells

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy, heat and water. They offer low to zero-emission power source for various applications from spacecraft to stationary power generation systems, automobiles, and small electronic devices. In principle, a fuel cell operates like a battery but it does not require recharging. It will produce electricity and heat as long as fuel is supplied. The concerns about pollutions in environment are the major factor that has influenced the fuel cell development. Due to high cost of the materials used in fuel cells such as the electrolyte membrane and noble metal-based electrocatalysts and durability of these systems are the most reasons why fuel cells do not popular for commercialization.

The first fuel cell was built in 1893 by Sir William Grove who pointed out that water could be split into hydrogen and oxygen by sending an electric current through it (a process called electrolysis). Grove hypothesized that electricity and water will be produced by reversing the electrolysis process. He created a primitive fuel cell and called it a gas voltaic battery. After experimenting with his new discovery, Grove proved his hypothesis. Fifty years later, scientists Ludwig Mond and Charles Langer invented the term fuel cell while attempting to build a practical model to produce electricity (Nice *et al.*, 2007).

2.1.1 Classification of Fuel Cells

Fuel cells can be classified into different ways according to the criteria used which are typically related to fuel cell operation or construction. In principle, six major types of fuel cells are classified as; alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC) and phosphoric acid fuel cell (PAFC). Based on the fuel used for the electricity generation, direct methanol fuel cell (DMFC) is further classified (Li, 2006). An overview of the fuel cell types is given in Table 2.1.

2.2 Electrochemical Reactions in PEMFC

Among the various types of fuel cell, polymer electrolyte membrane fuel cell (PEMFC) is the most promising candidate fuel cell system in terms of the simple operation and wide range of applications. In general, PEMFCs require humidified gases, hydrogen and oxygen (or air) as a fuel for their operation. The electrochemical reactions in fuel cell occur simultaneously on both anode and cathode sides of the cell. The cell operation of PEMFC is shown in Figure 2.1.

The basic electrochemical reactions of PEMFC in acidic medium are:

Anode:	$H_2 \rightarrow$	2H ⁺ +	2e ⁻	(1)
Cathode:	$\frac{1}{2}O_2 +$	2H ⁺ +	$2e^{-} \rightarrow H_2O$	(2)

Overall: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$



Figure 2.1 Schematic of PEMFC operation.

PEMFCs operate at relatively low temperatures, around 70-90°C. It requires a noble-metal catalyst (typically platinum) to separate the hydrogen into electrons and protons. As shown in Figure 2.1 hydrogen, which is fed to one side of cell and oxidized at anode, splits into protons and electrons. The protons travel through the polymer electrolyte membrane, while the electrons travel through electrically

(3)

Typcs of fuel cell	Fuel	Charge carrier in the electrolyte	Temperature (°C)	Efficiency (%)	Application	Advantages	Disadvantages
Alkaline fuel cell (AFC)	H ₂ pure	OH.	50–90	50-70	Space application	High efficiency	Intolerant to CO_2 in impure H ₂ and air, corrosion, expensive
Polymer electrolyte membrane fuel cell (PEMFC)	H ₂	H⁺	60–100	40-50	Vehicle & portable	High power density, low temperature	Intolerant to CO in impure H ₂ and expensive
Solid oxide fuel cell (SOFC)	CH ₄ , H ₂ , CO	O ²⁻	800-1000	50–60	Central, standalone & combined heat & power	High efficiency & direct fossil fuel	High temperature, thermal stress failure, coking & sulfur poisoning
Molten carbonate fuel cell (MCFC)	СН ₄ , H ₂ , СО	CO ₃ ²⁻	600–650	50-60	Central, standalone & combined heat & power	High efficiency, near commercial	Electrolyte instability, corrosion & sulfur poisoning
Phosphoric acid fuel cell (PAFC)	H ₂	H⁺	175–220	40-45	Standalone & combined heat & power	Tolerant to impure H ₂ , commercial	Low power density, corrosion & sulfur poisoning
Direct methanol fuel cell (DMFC)	СН₃ОН	H+	50-120	25-40	Vehicle & sınall portable	No reforming, high power density & low temperature	Low efficiency, methanol crossover & poisonous by product

Table 2.1 Characteristics of different types of fuel cell (Sopian et al., 2006)

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conductive electrode, current collectors and outside circuit where they perform useful work and return to other side of the cell. Oxygen is fed to cathode, which recombines with protons and electrons to produce water. The fact that fuel cell emits only clean water; fuel cell is thus a promising energy conversion system for the future.

In addition, PEMFC is similar to direct methanol fuel cell (DMFC), a type of fuel cell, which uses methanol as the fuel instead of hydrogen. The cell operation of DMFC is shown in Figure 2.2.

The basic electrochemical reactions of DMFC in acidic medium are:

Anode: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$ (4)

 $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$

Cathode:
$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$
 (5)

Overall:



Figure 2.2 Schematic of DMFC operation with a polymer electrolyte membrane as the electrolyte.

2.3 Composition of PEMFC

The major component of PEMFC consists of two electrodes which are anode and cathode. Both of them are separated by polymer electrolyte membrane as shown in Figure 2.3. Each electrode is comprised of gas diffusion layer (GDL) and catalyte layer in which the catalyte layer is placed between GDL and the polymer membrane.

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Membrane electrode assembly (MEA) refers to a system which the gas diffusion layer, catalyst layers and polymer electrolyte membrane are bound together.



Figure 2.3 Schematic of a single typical polymer electrolyte membrane fuel cell (Litster *et al.*, 2004).

2.3.1 Membrane

A fuel cell membrane must exhibit relatively high proton conductivity, excellent electronic insulator, low gas permeability and must be chemically and mechanically stable in the fuel cell environment. Membrane materials for PEMFC can be classified as perfluorinated ionomers, partially fluorinated polymers, non-fluorinated membranes with aromatic backbone, non-fluorinated hydrocarbons, acid–base blends (Smitha *et al.*, 2005). Scheme 2.1 gives some example of the membrane materials used for fuel cells.



Scheme 2.1 (Smitha *et al.*, 2005)

The membrane systems are different in terms of the structure, the physical properties and their in situ performances as summaried in Table 2.2.

The most widely used membranes for PEMFC are perfluorosulfonic acid based material ones. The chemical structure is perfluorovinyl ether side group with tetrafluoroethylene backbone terminated with sulfonate groups. The best known is Nafion[®] made by DuPont. Similar materials have been developed as a commercial product by other manufacturers such as Asahi Glass (Flemion[®]), Asahi Chemicals (Aciplex[®]), and Dow Chemical (Dow). The chemical structures of these perfluorosulfinic acids are illustrated in Figure 2.4.

$$\xrightarrow{(CF_2-CF_2)_{x}(-CF_2-CF)_{y}}_{(O-CF_2-CF)_{m}} \xrightarrow{(CF_2)_{n}}_{(CF_3)} SO_3H$$

Figure 2.4 Structure of commercial perfluorosulfonic acid polymers. Nafion[®] (DuPont): m=1; n=2; x=5-13.5; y=1, Flemion[®] (Asahi Glass): m=0,1; n=1-5; x=5-13.5; y=1, Aciplex[®] (Asahi Chemicals): m=0; n=2-5; x=1.5-15; y=1, Dow (Dow Chemical): m=0; n=2; x=3.6-10, y=1 (Li, 2006).

Table 2.2 Structure-property relationships and in situ performance of polymers(Smitha et al., 2005)

Category	Structure	Physical properties	In situ performances
Perfluorinated	Fluorinated	 Membranes are 	• Membrane is durable up to
(pf)	backbone like PTFE	strong and stable in	60,000 h
membranes	• Fluorocarbon side	both oxidative and	• Proton conductivities in well
	chain	reductive	humidified membranes are
	Ionic clusters	environments	0.2 S/cm at PEMFC operating
	consisting of sulfonic		temperatures
	acid ions attached to		• Cell resistance of 0.05 Ω cm ²
	the side chains		for 100 μm thick membrane
			with voltage loss of only 50
			mV at 1 A/cm ² is achievable
Partially	Fluorocarbon	Membranes are	Less durable than
fluorinated	Hydrocarbon or	relatively strong in	perfluorinated ones
membrane	aromatic side chain	comparison to pf	Low performance
	grafted onto the	membrane, but	• On suitable modification,
	backbone, which can	degrade fast	yield membranes with
	be modified base		comparable proton
			conductivities
Non	• Hydrocarbon base,	 Membranes posses 	Poor conductors of protons
fluorinated	typically modified	good mechanical	• Exhibit low durability on
hydrocarbon	with polar groups	strength	account of swelling obtained
membranes		• Poor chemical and	by incorporation of polar
	÷	thermal stability	groups into the polymer matrix
Non-	• Aromatic base,	Good mechanical	 Good water absorption
fluorinated	typically modified	strength	Relatively high proton
aromatic	with polar / sulfonic	Chemically and	conductivity is attainable
membranes	acid groups	thermally stable even	Conductance of SPPBP at
	9	at elevated	65 mol% of sulfonation is
	1.1	temperatures	10^{-2} S/cm that is retained at
			temperatures above 100 °C
Acid-base	• Incorporation of acid	• Stable in oxidizing,	Good dimensional stability
blend	component, into an	reducing and acidic	• Exhibit proton conductivity
membranes	alkaline polymer base	environments	comparable to Nafion [™]
		• High thermal.	• Durability of the membranes
		stability	is still to be proven

Such perfluorosulfonic acid membranes exhibit high proton conductivity and good chemical stability at the temperature lower than 80°C. The limitations of these membranes are poor proton conductivity at high temperature, low humidities, poor resistance to methanol transport, and high cost.

In addition, extensive research has been done to produce less expensive membranes and to compensate the various problems occurred with perfluorosulfonic acid membrane. Polymer electrolyte membranes based on hydrocarbon polymer have been developed including sulfonated aromatic polymers, alkylsulfonated aromatic polymers and acid-base polymer complexes (Rikukawa *et al.*, 2000). Some of these hydrocarbon polymers such as sulfonated poly(ether ether ketone) [PEEK], sulfopropylated polybenzimidazole [PBI], sulfonated polycarbonate [PC], sulfonated poly(phenylene oxide) [PPO], sulfonated polyimide [PI], sulfonated polysulfone [PSU], sulfonated poly(phenylene sulfide) [PPS] and sulfonated poly(phenyl sulfone) [PPSU] are illustrated in Figure 2.5.



Sulfonated PPSU

Figure 2.5 Chemical structures of polymer electrolyte membrane based on hydrocarbon polymers.

2.3.2 Electrode

A fuel cell electrode composed of catalyst layer and gas diffusion layer (GDL) which be made of backing layers, microporous layers and catalyst layers. The electrochemical reactions occur at the catalyst surface at the interface between the membrane and the GDL in both anode and cathode.

GDLs are used to collect the electrical current generated within the cell. In addition, GDL must be sufficient porous to allow the reactant gases and water pass through. Typically, GDL is usually made of carbon powder mixed with hydrophobic agents such as polytretafluoroethylene (PTFE) to bind carbon particles into a layer and avoid water flooding of the electrodes. However, GDL must be fitted to the catalyte layer and electronic conductor, to ensure the best electrical contact of the cell.

The most common catalyst used in PEMFC for both oxygen reduction and hydrogen oxidation reactions is platinum (Pt). In general, Pt catalysts loading in cathode are usually higher than loading in anode because of the slow rate of oxygen reduction catalysis on cathode.

At the first time, the catalysts used in PEMFCs are made of pure platinum or Pt black. Due to very high cost of Pt catalysts loading in catalyst layer, many researchers have developed other strategies to reduce the Pt level for the past decade. The effectively active surface of Pt catalysts can be achieved by using small Pt particles dispersed to maximize the catalyst utilization in the reactions. A successful method is to use carbon-supported Pt catalyst in which different amount of Pt can be deposited on larger carbon surface (Xiong *et al.*, 2005). For example, 10% Pt/C catalyst implies that in the platinum and carbon mixture consists of 10% of Pt and 90% of carbon by weight (or mass). Typically, the catalyst layer in MEAs usually composed of carbon-supported Pt and PTFE as well as Nafion, which is used as binding agent and water rejection.

In practical, fuel stream is usually contaminated with carbonmonoxide (CO), which can cause poisoning in the anode of low temperature fuel cell such as PEMFC. CO poisoning occurs due to the absorption of CO on the active sites of Pt catalyst so that no sites are available for reaction with hydrogen. Pt-based metal

alloys have been developed to reduce CO poisoning in the anode (Sasaki *et al.*, 2004) and to enhance the activity of oxygen reduction reaction for fuel cell (Xiong *et al.*, 2005). Some examples of bifunctional catalysts have been investigated including alloys of Pt with Ru, Fe, Mo, Cu, Os, Co, Sn and Re, etc.

2.4 Membrane Electrode Assembly (MEA)

There are two modes of MEA assembly: (1) application of catalyst layer to GDL followed by membrane addition or (2) application of catalyst layer to membrane followed by GDL addition, however, the catalyst layer can be prepared and applied in two separate steps or using a single sputtering process. In addition, several manufacturing options exist within these two modes of MEA manufacturing as shown in Scheme 2.2 (Mehta *et al.*, 2003).



Scheme 2.2 (Mehta et al., 2003)

Mehta *et al.*, (2003) summarized the current processing steps and primary inputs and outputs for catalyst preparation and application in two steps or by sputtering as shown in Tables 2.3 and 2.4.

Table 2.3 Analysis of catalyst preparation and application for MEA assembly mode1: application of catalyst to GDL (Mehta *et al.*, 2003)

Processing steps	Primary inputs	Primary process outputs		
Catalyst preparation and appl	ication: spreading method			
1.Dough making	Carbon supported metal-catalyst, PTFE	Dough		
2. Spreading	Dough, wet-proofed GDL	Coated GDL		
3. Rolling	Coated GDL	GDL/catalyst assembly		
Catalyst preparation and appl	ication: spraying method			
1.Composite mixture making	Carbon supported metal-catalyst, water, PTFE, alcohol	Mixture for spraying		
2. Spraying	Mixture, wet-proofed GDL	Coated GDL		
3. Sintering	Coated GDL	Coated and sintered GDL		
4. Rolling	Coated and sintered GDL	GDL/catalyst assembly		
Catalyst application: catalyst powder deposition method				
1.Mixing	Carbon supported metal-catalyst, PTFE	Reactive powder		
2. Powder application				
2.1 Using a line funnel under gravity	Powder, wet-proofed GDL	Coated GDL		
or				
2.2 Horizontal powder application	Powder, wet-proofed GDL	Coated GDL		
3. Rolling	Coated GDL	GDL/catalyst assembly		
Catalyst preparation and appl	ication:: ionomer impregnation metho	od		
1. Mixing	Carbon supported metal-catalyst, PTFE, PFSA in aliphatic alcohols and water	Catalyst solution		
2. Painting Sputtering	Catalyst solution, wet-proofed GDL	GDL/catalyst assembly		
1.Sputtering 2. Rolling	Wet-proofed GDL, metal catalyst Sputter deposited paper	Sputter deposited paper GDL/catalyst assembly		

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Table 2.4 Analysis of catalyst preparation and application for MEA assembly mode2: application of catalyst to membrane (Mehta *et al.*, 2003)

Processing steps	Primary inputs	Primary process outputs			
Catalyst preparation and application: impregnation reduction method (electroless deposition method)					
1. Platinum salt impregnation	Membrane, $(NH_3)_4$ PtCl ₂ (aq)	Membrane loaded with metal salt			
2. Reduction of $(NH_3)_4Pt^{2+}$	Membrane loaded with metal salt, NaBH ₄ (aq)	Membrane/catalyst assembly			
Catalyst preparation and applic	ation: evaporative deposition				
1. Metal salt evaporation	Membrane, heat, metal salt such as (NH ₃) ₄ PtCl ₂ (aq)	Membrane impregnate with metal salt			
2. Reduction of Metal salt	Membrane impregnate with metal salt, NaBH ₄ (aq)	Membrane/catalyst assembly			
Catalyst preparation and applic	ation: evaporative deposition				
1. Composite powder making	Metal-catalyst supported C, PTFE, membrane material	Composite powder .			
2 Atomization	powder Composite powder	Atomized neuros			
3 Dry spraying	Atomized powder membrane	Coated membrane			
4. Hot rolling	Coated membrane	Membrane/catalyst assembly			
Catalyst preparation and applic	ation: novel fabrication method				
1. Catalyst preparation	PFSA, metal-catalyst	PFSA coated catalyst			
2. Vacuum drying	PFSA coated catalyst	Dried catalyst			
3. Mixing catalyst with other elements	Catalyst, PTFE, CaCO ₃ , water	Composite mixture			
4. Filtration	Composite mixture	Filtration			
5. Rolling	Filtration	Rolled sheet			
6. CaCO ₃ removal	HNO ₃ , sheet	CaCO ₃ free sheet			
7. Drying	Sheet	Electrode catalyst assembly			
8. Hot pressing at 150 °C	Electrode catalyst assembly, membrane	Membrane/catalyst assembly			
Catalyst preparation and application: catalyst decaling method					
1. Mixing	Metal-catalyst supported C,	Metal ink			
2. Conversion of ink to TBA+	Metal ink, TBAOH	TBA+ ink			
3. Apply TBA+ ink to PTFE	TBA+ ink, PTFE blank	Coated blank			
4 Drying	Coated blank	Dried blank			
5. Hot press to Na ^{$+$} membrane	Membrane, dried blank, heat	Membrane/blank assembly			
6. Peel of blank	Membrane/blank assembly	Coated membrane			
7. Protonation	Coated membrane, boiling H₂SO₄	Protonated membrane			
8. Rinsing	Deionized water, membrane	Clean, protonated membrane			
9. Air drying	Clean, protonated membrane	Membrane/catalyst assembly			

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Processing steps	Primary inputs	Primary process outputs			
Catalyst preparation and application: painting method					
 Painting of ink on Na⁺ polymer electrolyte membrane 	TBA+ ink, Na ⁺ membrane	Coated membrane			
2. Oven dry in a vacuum table	Heat, coated membrane	Semi-dried coated membrane			
3. Rapid heating	Semi-dried membrane	Dried coated membrane			
4. Protonation	Coated membrane, boiling H_2SO_4	Protonated membrane			
5. Rinsing	Deionized water, membrane	Clean, protonated membrane			
6. Air drying	Clean, protonated membrane	Membrane/catalyst assembly			
Sputtering					
1. Mixing	PFSA solution, carbon powder, Isopropyl alcohol	Ion conducting polymer ink			
2. Sputtering	Membrane	Sputtered membrane			
3. Brushing	Ion conducting polymer ink,	Coated membrane			
4. Repeat 2 and 3	sputtered membrane	Membrane/catalyst assembly			

2.5 Background of Host-Guest Complex

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The support materials play an important role for the metal particles to be highly dispersed and stable. Various supported material such as Valcan XC-72 (Lizcano-Valbuena *et al.*, 2003), polyimide resin (Akamatsu *et al.*, 2003), cellulose diacetate (Huang, *et al.*, 2005) and polymer metrices (Zhou *et al.*, 2002) have been developed to improve the catalytic efficiency.

Akamatsu *et al.*, (2003) used polyimides as the host material to control the size and the distribution of monodispersed cupper nanopaticle. These monodispersed copper nanoparticles in polyimide resin could be prepared by modifying the polyimide resin surface with KOH to form carboxylic groups in the modified layer through imide ring-cleavage reactions. Then, the copper ion complexation achieved by ion exchange with the bound potassium ions followed by reducing in hydrogen atmosphere to yield metallic nanoparticles. Figure 2.6 shows an idea about the synthesis process for composite polyimide layers containing monodispersed copper nanoparticles.





Host molecules can be also used as support materials. A few example of host-guest complex used in fuel cell application such as iron (III) tetramethoxyphenylporphyrins chloride (FeTMPP-Cl) (Schulenburg *et al.*, 2003) and cobalt tetramethoxyphynylporphyrin (CoTMPP) (Ma *et al.*, 2006) have been investigated for promoting oxygen reduction reactivity at the cathode in DMFCs and PEMFCs (Figure 2.7).



FeTMPP-Cl

CoTMPP

Figure 2.7 Chemical structures of iron (III) tetramethoxyphenylporphyrin chloride (FeTMPP-Cl) and cobalt tetramethoxyphynylporphyrin (CoTMPP).

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The present work proposes a new MEA concept for fuel cell applications by using host-guest complexes for enhancement Pt utilization and dispersion of Pt in catalyst layer. The host molecules are N,N-Bis(2-hydroxybenzyl)alkylamine (HBA) derivatives, which exhibit themselves as host to accept guest such as copper ion (Phongtamrug *et al.*, 2006) under the double-oxygen-bridged dimeric system in which the host-guest interaction is based on a charge-transfer coordination. Figure 2.8 demonstrates the supramolecular structure of HBA with Cu framework.



Figure 2.8 Supramolecular structure of *N*,*N*-Bis(2-hydroxybenzyl)alkylamine (HBA) with Cu framework (Phongtamrug *et al.*, 2006).

2.6 Motivation of Present Work

The performance of PEMFC is critically dependent on the activity of the precious metal catalyst such as Pt and Pt alloys catalyst. The conventional method for MEA fabrications is limited by an ineffective distribution of catalyst in three phase boundaries in which the electrolyte, reactants and conductive carbon are in a close contact with the catalyst. An approach to improve the Pt utilization is impregnate the proton conducting polymer such as Nafion into Pt/C catalyst layer since the ionic and electronic contacts are essential components for the high Pt catalyst utilization (Lee *et al.*, 1998).

However, most researches show that Pt nanopaticles tend to aggromerate or detach from carbon support, as shown in Figure 2.9, after PEMFC operation.



Figure 2.9 Pt agglomeration and Pt detachment from support material surface after PEMFC operation (Shao *et al.*, 2007).

Luo *et al.*, (2006) observed that Pt particles aggregate and the Pt content in the catalyst layer significantly decreases after the 200 h performance. Figure 2.10 are TEM micrographs of the original Pt/C catalyst and the degraded catalyst.



Figure 2.10 TEM micrographs of Pt/C catalyst a) original Pt/C catalyst and b) after degradation (Luo *et al.*, 2006).

There, if the molecules with metal ion encapsulated can be aligned at the interface, we can expect the full catalysts activity with sustainability. In order to achieve that ideal case, the present work aims to show the possibility of embedding catalyst layer via supramolecular structure. The supramolecules with catalyst at the interface are expected to provide several advantages such as the high active site, the prevention of agglomeration, and good distribution of the catalyst. This approach is considered as a novel effective way to initiate the function of the catalyst in the MEA (Figure 2.11).



Figure 2.11 Membrane electrode of a PEMFC and an overview of the present work.