CHAPTER II
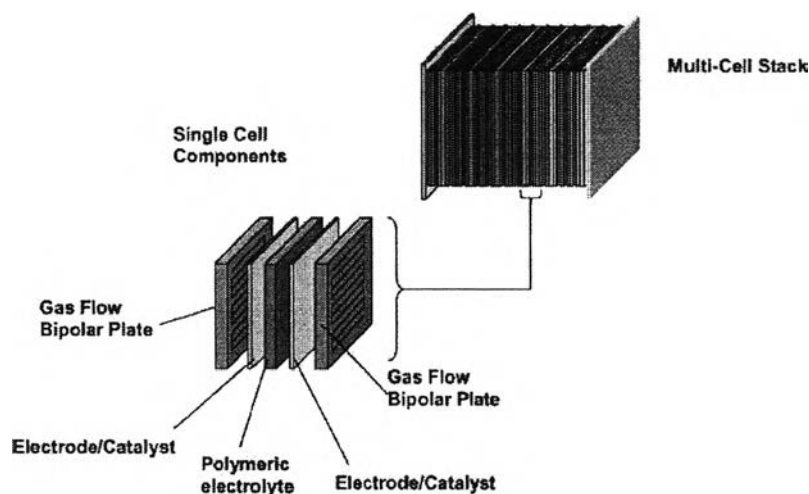# LITERATURE REVIEW

2.1 Proton Exchange Membrane Fuel Cell (PEMFC) and its Compartments

Proton exchange membrane fuel cells (PEMFCs) have extended to the state of being the head among the different types of fuel cells. The PEMFC was the first types of the fuel cells to find the applications for the power source for NASA's Gemini Space Flights in 1960s (Maget, 1968 and Bockris and Srinivasan, 1969). Through the dormancy of this technology for about 20 years thereafter, the California Environmental Legislations and the USA partnership for a New Generation of Vehicles Program (PNGV), initiated in 1993 and sponsored by the US government and the big three US automobile manufacturers, stimulated its worldwide resuscitation for the transportation applications and gave birth to the R&D programs for the portable power and power generation applications. For more than a decade later, the partial commercializing stage was reached. In 2005 in Monaco, five kinds of power cars with an onboard PEMFC system (fuel cell vehicle (FCV)) introduced by GM, Hyundai, Daimler-Chrysler, etc. ran into a road rally covering the distance of approximately 410 km through Switzerland for the journey time of 6 h with one re-fuelling stop. This rally clearly showed the present status of the applications of PEMFC for the FCV field (Jung, 2007).

Scheme 2.1 illustrates the main compartments of a PEMFC power source: (i) the single cell composed of the porous gas diffusion electrodes (anode and cathode), the proton conducting membrane, anodic and cathodic catalyst layers, which are mostly deposited on the electrode but more recently in some works on the proton conducting membrane, and current collectors with the reactant flow fields; (ii) a stack of cell in series with the current collectors also serving as the bipolar plates; (iii) cell stacks (modules) connected in series or parallel, depending on the voltage and current requirements for specific application; and (iv) needed auxiliaries for thermal and water management and for gas compression.

Scheme 2.1 Fuel cell and stack

Single Cell
Components

Multi-Cell Stack

Gas Flow
Bipolar Plate

Gas Flow
Bipolar Plate

Electrode/Catalyst

Polymeric
electrolyte

Electrode/Catalyst

The unique feature of the PEMFC as compared with other types of fuel cells (except for solid oxide fuel cell) is the usage of solid polymer electrolyte membrane. PEMFC operates at low temperature (below 100 °C) and generate a specific power ($W\ kg^{-1}$) and power density ($W\ cm^{-2}$) higher than any other type of fuel cell. It is the reason that the PEMFC has received much attention to be a candidate power source for transportation, small-scale power generation and portable power. There are two types of PEMFC divided by the anodic fuel used, i.e., polymer electrolyte fuel cell (PEFC) supplied with humidified hydrogen gas and direct methanol fuel cell (DMFC) with methanol aqueous solution.
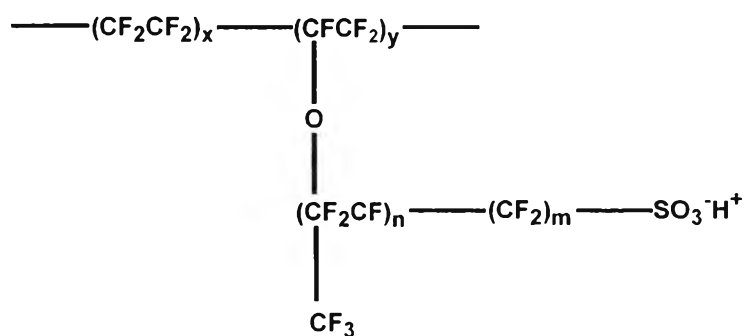
2.2 Polymer Electrolyte Membrane (PEM)

2.2.1 Background

One of the most important parts in the single cell of PEMFC as enumerated before is the polymer electrolyte membrane (PEM) playing a significant role as a proton conducting pathway and a barrier for the reactant gases. The evaluation of the membranes for fuel cell applications started as early as 1959 by GE with the testing of phenolic membranes, prepared by the polymerization of phenol-sulfonic acid with formaldehyde. These membranes had low mechanical strength and short lifetime of 300-1000 h as well as a low power density of 0.05-0.1 $kW\ m^{-2}$

(Maget, 1968). During 1962-1965, GE pushed more effort to increase the power density by developing the partially sulfonated polystyrene sulfonic acid membranes prepared by dissolving sulfonic acid in ethanol-stabilized chloroform and sulfonating at room temperature. The membrane with the better water uptake and power density of 0.4-0.6 kW m^{-2} was obtained and enabled for the application in NASA's Gemini Flights. Thereafter, in the late sixties, the cross-linked polystyrene-divinylbenzene sulfonic acid in an inert matrix was developed. This membrane showed very good physical properties with the life of the membrane ranging from 10^3-10^4 h and provided the power density of 0.75-0.8 kW m^{-2}.

The main problems encountered with all the above mentioned types of PEMs were that: (i) the proton conductivities were not sufficiently high to reach a power density even as low as 100 mW cm^{-2}; and (ii) oxidation of the C-H bonds occurred in the membranes due to the high potential of the PEMFC cathode, as well as by hydrogen peroxide, often formed at the anode by small amount of crossover from the cathode to the anode in PEMFC (Costamagna et al., 2001). In 1970, the membrane replacement for the better PEMFC performance from the phenol sulfonic acid and the polystyrene sulfonic acid to a Du Pont's perfluorosulfonic acid membrane called "Nafion®" was due to the two reasons. Firstly, the structure of Nafion®, which is similar to Teflon, has side chains with ether linkages followed by CF$_2$ groups and ended with sulfonic acid groups (Scheme 2.2).

Scheme 2.2 Structure of Nafion®

$$\text{---}(CF_2CF_2)_x\text{-----}(CFCF_2)_y\text{---}$$
$$|$$
$$O$$
$$|$$
$$(CF_2CF)_n\text{-----}(CF_2)_m\text{-----}SO_3^-H^+$$
$$|$$
$$CF_3$$

The high electronegativity or electron affinity of the fluorine atom, bonded to the same carbon atom as the SO_3H group, makes the sulfonic acid to be a super acid and resulting in approximately a two-fold increase in the specific proton conductivity, e.g., 90-120 mS/cm at 80 °C in relative humidity (RH) range of 34-100 % (Samms *et al.*, 1996). Secondly, the CF_2 groups are highly stable at the potential of the oxygen cathode and also the hydrogen peroxide from anode. This provides the prolongation of the PEMFC lifetime at least by four orders of magnitude (10^4-10^5 h). The Dow Chemical Company and the Asahi Chemical Company synthesized advanced perfluorosulfonic acid membranes with shorter side chain and higher ratio of SO_3H to CF_2 groups (Wakizoe *et al.*, 1995). The lower equivalent weight of these membranes as compared to Nafion® provides the higher specific proton conductivity enabling significant improvement in PEMFC performance (Figure 2.1), i.e., about 50-100 mV increase in cell potential at 1 A cm^{-2} over that on the control Nafion® 115 with the same thickness of 100 µm (Costamagna and Srinivasan, 2001).
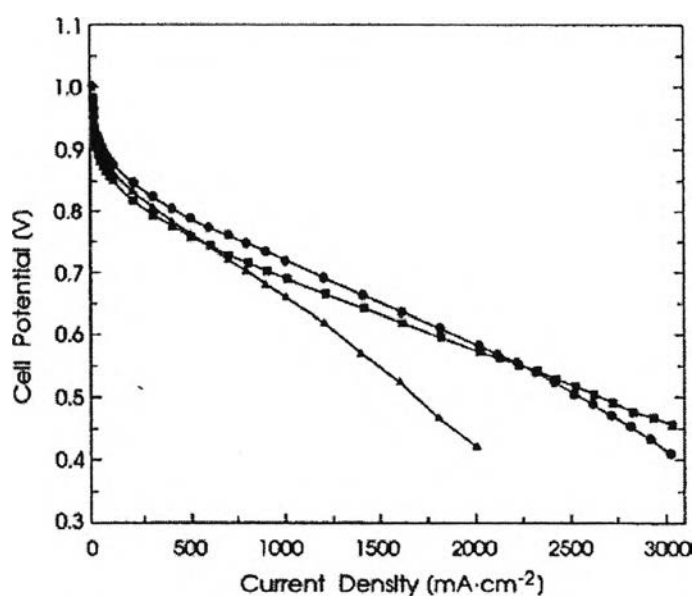
Figure 2.1 Effect of different proton conducting membranes, Nafion®-115 (▲), Aciplex-S® 1004 (●), and Dow (■), on PEMFC performance: H_2/O_2 reactants (E-TEK electrodes, 20 % Pt/C, 0.4 mg Pt / cm^2); 95 °C; P=5 atm.

2.2.2 Requirements for PEM

Since the PEM is the core compartment of the PEMFC, in order to achieve the high fuel cell efficiency, the PEM must possess the following desirable properties:

- high proton conductivity to support high current with minimal resistive losses and zero electronic conductivity;

- adequate mechanical strength and stability;

- chemical and electrochemical stability under operating conditions;

- moisture control in stack;

- extremely low fuel or oxygen or co-catalyst, such as ruthenium in the case of DMFC, crossover to maximize coulombic efficiency;

- production cost compatible with intended application;

- operating at elevated temperature.

2.3 Evaluation of PEM

2.3.1 Water Uptake

Proton conductivity and water uptake through the Nafion® and other sulfonated non-perfluorinated membranes are relied on the microstructure of the membrane, i.e., ion cluster size (Kim *et al.*, 2006). The water uptake in the membrane is usually evaluated as follows: (i) immersing the membrane in distilled water at room temperature for 48 h and weighted to obtain W_w; (ii) drying the wet membrane under vacuum at 80 °C for 24 h to obtain dry membrane (W_d); and (iii) calculating the water uptake from the weight differences between wet and dry membranes using following equation:

$$\text{Water Uptake} = \left(\frac{W_w - W_d}{W_w} \right) \times 100$$

In addition, the water uptake is also evaluated by thermogravimetric analysis. The water content in the membrane is considered as the percent weight loss

of the hydrated membrane at the temperature range of 60-150 °C which is the water evaporation temperature.

2.3.2 Ion Exchange Capacity (IEC)

The efficiency of proton transferring through the membrane depending on the number proton exchangeable groups, or so-called ion exchange capacity (IEC) of the membrane is an important factor.

By trating the solution obtained with 0.1 N NaOH solution using phenol red as the endpoint indicator, IEC can be calculated. The volume of NaOH solution needed is expressed it in term of milliequivalent of exchanged proton per dry polymer weight (meq_{H+}/g) (Basile *et al.*, 2006).

2.3.3 Gas Permeabilty

The gas permeation is one of the important parameters of the membranes used in PEMFCs since the low gas feed crossover through the membrane results in the high efficiency of the fuel cells.

Scheme 2.3 Schematic draw for gas permeability measurement
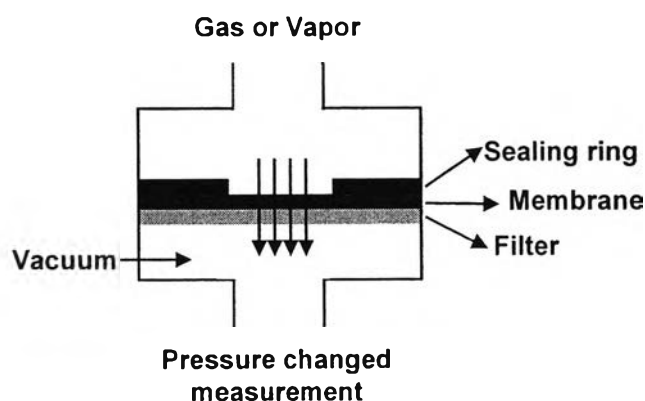
From the schematic draw illustrated the gas permeation measurement system (Scheme 2.3), the membrane under test is placed in between the filter and sealing ring when the feed side is supplied by gas or vapor with the vacuum permeate side. The gas permeability is measured by the pressure changed at the permeate side.

The gas permeation is expressed by the gas permeability coefficient, P, and can be calculated as follow (Jansen *et al.*, 2007):

$$P = \frac{L \times V_p \times V_m}{A \times T \times \Delta P \times R} \left(\frac{dP}{dt} \right)$$

Where L is the membrane thickness (cm), V_p is the permeate volume (cm^3), V_m is the molar volume of the gas at standard temperature and pressure, A is the membrane surface area (cm^2), T is the absolute temperature (K), ΔP is the pressure difference between feed and permeate part (cmHg) and dP/dT is the changing rate of permeate pressure (cmHg/s).

2.3.4 Methanol Permeability

In the case of the membranes used in DMFC systems, the ability to be a barrier not only for gas permeation and electron transferring but also for methanol crossover is considered. Methanol permeability and excessive swelling in alcohol environment cause an over potential at cathode and the decrease in mechanical strength, respectively (Li *et al.*, 2003). In general, the methanol permeability through the membrane is determined by either diffusion or pervaporation system. From Scheme 2.4, the diffusion system composes of two compartments with the test membrane in between.

**Scheme 2.4** Diffusion system

Stirrer bar
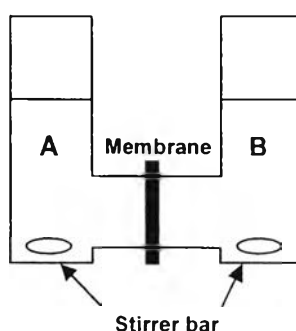
Compartment A is filled with methanol solution while compartment B is with water. The sample solutions from both compartments are taken at 1-1.5 h interval of time.

The methanol concentration in each solution is analyzed by gas chromatograph (GC). The methanol permeability, P (cm^2/s), is calculated as the following equations (Jiang *et al.*, 2006).

$$P = \frac{V_B \times L \times \dfrac{dC_{B(t)}}{dt}}{C_A \times A}$$

where C_A and C_B are the methanol concentration in the compartments A and B (%(v/v)), respectively, t is the permeation time (s), A is the exposed area of the membrane (cm^2), L is the thickness of the membrane (cm) and V_B is the solution volume of the compartment B.

Scheme 2.5 Pervaporation system
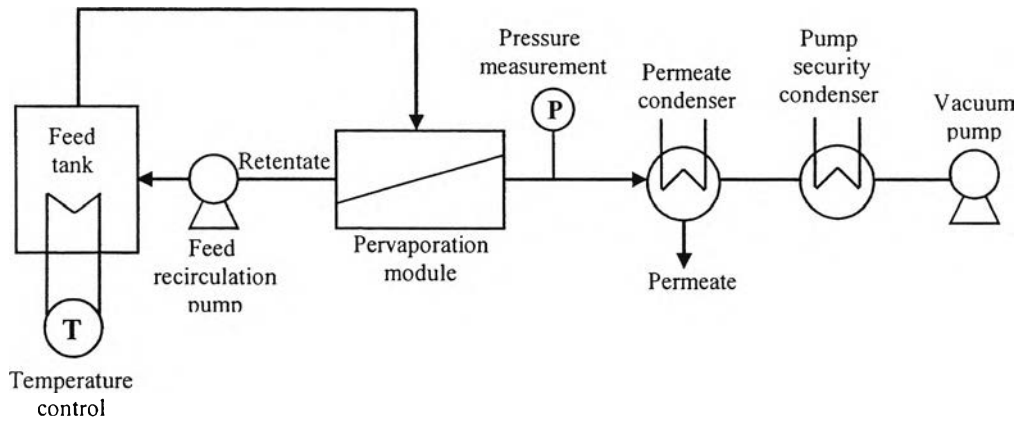
In the case of pervaporation system (Scheme 2.5), the tested membrane is placed in between the feed chamber with circulated methanol, at the same time, the permeate side is evacuated. The permeated vapor is collected under the liquid nitrogen in every 1-1.5 h. The permeate is weighted and analyzed by gas chromatograph. The methanol permeability is estimated by the following equations based on the total (J_{tot}) and methanol (J_{MeOH}) fluxes.

$$J_{tot} = \frac{W_{perm} \times L}{t \times A}$$

$$J_{MeOH} = \frac{J_{tot} \times C_{MeOH}}{100}$$

Where W_{perm} is the weight of permeated methanol solution, L and A are thickness and surface area of the membrane, respectively, t is permeation time and C_{MeOH} is methanol concentration.

2.3.5 Proton Conductivity

In order to evaluate the electrical property based on the proton conductivity of the membrane, the complex impedance is measured by applying alternating current with various frequencies. The typical impedance response (Z_{im}-Z_{re} plot) is achieved (Figure 2.2).
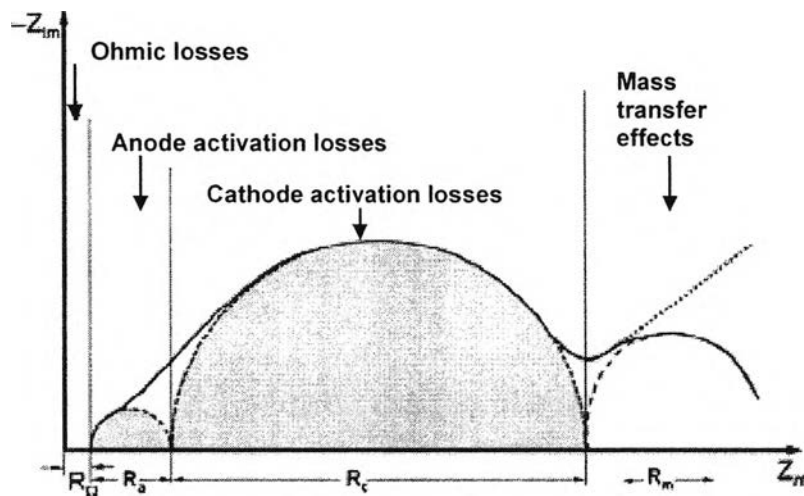

Figure 2.2 Impedance plot (Z_{im}-Z_{re}) of hypothetical PEM fuel cell stack and four losses in the system (Zhu *et al.*, 2007).

For our research works, the proton conductivity measurements considered in this present work are based on two systems, i.e., anhydrous and humidity control systems. The proton conductivity of the hydrated membranes is measured without moisture feeding in the case of anhydrous system whereas that of humidity control system is carried out with 100 % relative humidity as the instruments and equipments shown in Scheme 2.6 (a) and (b).

Scheme 2.6 Instruments and equipments for proton conductivity measurement with anhydrous (a) and humidity control systems (b)
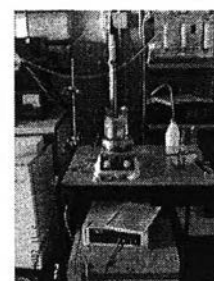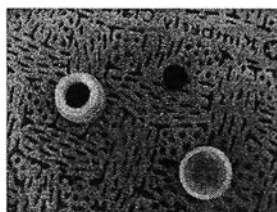
(a)
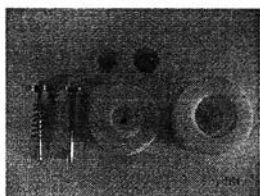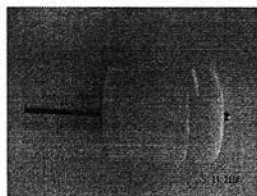
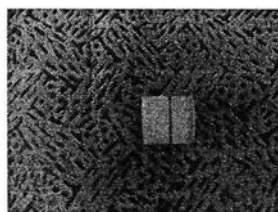**Impedance chamber**   **Impedance spectrometer**

(b)

Impedance chamber with humidity control   **Impedance
spectrometer**

     The proton conductivity, σ, is calculated from the complex impedance values at various temperatures based on $\sigma = L/RA$, where L and A are the thickness and surface area of the membrane, respectively. The bulk resistant of the membrane, R, is obtained from the intersection of Z_{re} axis (Wintersgill and Fontanella, 1998). Proton conductivity is usually reported by the plot versus temperature, relative humidity, ion exchange capacity, water uptake or additive content. For example the plot between proton conductivity and temperature of poly(diphenylether-1,3,4-oxadiazole) with different IEC under 100 % relative humidity is as shown in Figure 2.3.
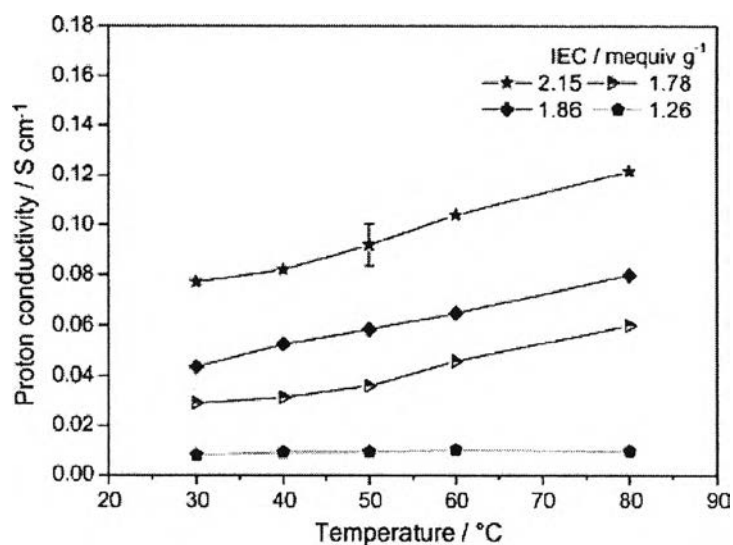
**Figure 2.3** Proton conductivity versus temperature of poly(diphenylether-1,3,4-oxadiazole) with different IEC (Gomes *et al.*, 2008).
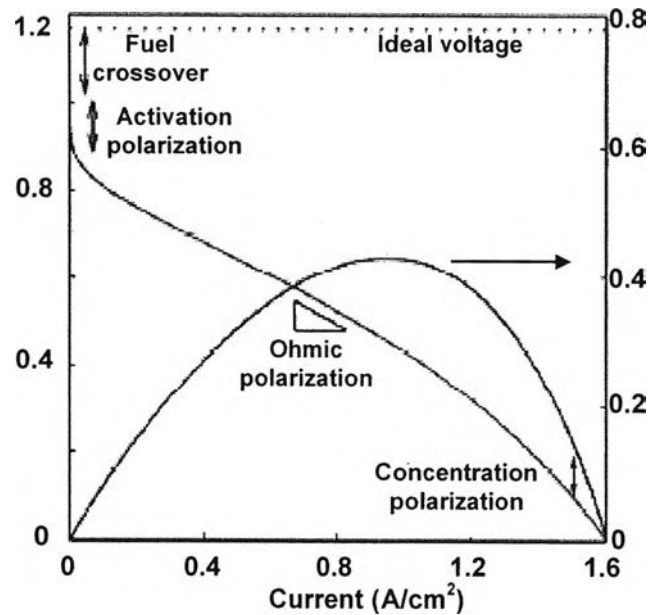
2.3.6 Single Cell Performance

As fuel cells are electrochemical devices that convert the chemical energy of redox reaction directly into electric energy, the performance of the fuel cells based on the generated electricity and voltage is evaluated by single cell test either with humidified hydrogen gas or methanol aqueous solution for anode supplying. Here, our research works have focused on the electrolyte membrane preparation and fuel cell performance evaluation from our synthesized membrane; thus, we have used all other components from the confidential fuel cell products, such as bipolar plates and single cell test station from ElectroChem, Inc., Nafion 117® reference membrane from Ion Power, Inc. and electrodes from E-TEK to precisely estimate the performance of our synthesized membranes. Membrane electrode assembly (MEA) is prepared by the compression with temperature and pressure (80 °C and 2 tons, respectively) of the membrane in between two electrodes. In the case of hydrogen-based PEMFC, Pt black electrodes loaded on the carbon cloth are used for both electrodes while those of DMFC are Pt-Ru alloy for anode and Pt black for cathode. Thereafter, the MEA is put together with the bipolar plates and gas diffusion layers (GDLs) to obtain the single fuel cell as all procedures shown in Scheme 2.7.

Scheme 2.7 Membrane electrode assembly (MEA) preparation, single cell and instruments for fuel cell performance evaluation

MEA preparation

Single cell and instruments for fuel cell performance evaluation
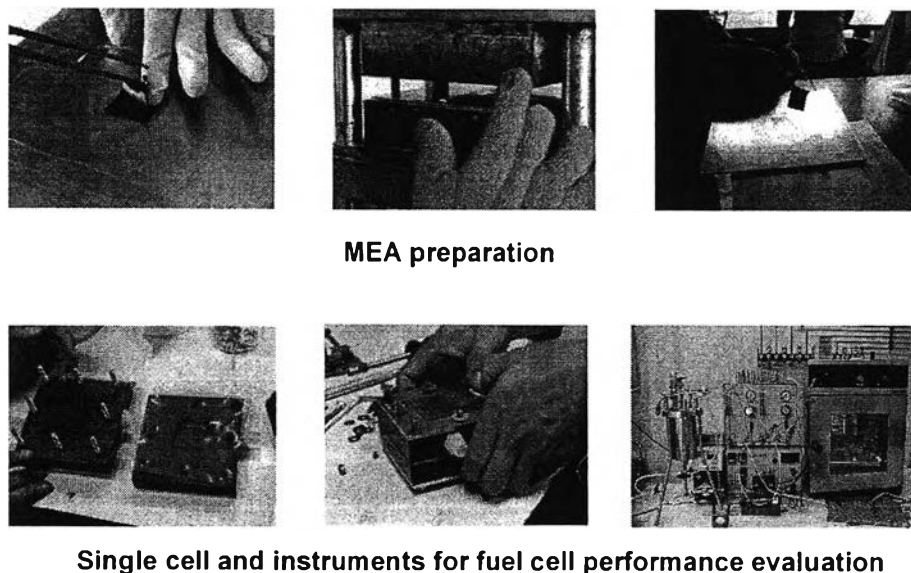
The current and voltage generated from the single cell are measured and revealed as the plot of voltage and power density versus current density named as polarization curve shown in Figure 2.4 which belongs to hydrogen-based fuel cell system. Based on theory, the standard potential (E°) obtained from a fuel cell in which hydrogen and oxygen reaction is 1.229 V (Williams, 2002). From Figure 2.4, the open circuit voltage (OCV) supposed to be about 1.23 V; however, due to the crossover of the fuel, the OCV value is decreased. Besides, the actual potential is continually decreased from its equilibrium potential because of irreversible losses. The losses, which are called polarization, overpotential or overvoltage, originate primarily from three sources: (i) activation polarization; (ii) ohmic polarization; and (iii) concentration polarization. These losses result in the cell voltage which is less than the ideal potential, E (E = E°-E$_{losses}$).

1.2 Fuel crossover Ideal voltage 0.8

Activation polarization 0.6

0.8

0.4 Ohmic polarization

0.4 0.2

Concentration polarization

0 0
0 0.4 0.8 1.2 1.6
Current (A/cm²)

Figure 2.4 Polarization curve of hydrogen based fuel cell system (Williams, 2002).

Activation polarization is directly related to the rate of electrochemical reaction. The slow reaction kinetic rate occurs at the electrocatalyst is dominant for this loss. In the case of ohmic polarization, the potential losses arise because of resistance to flow of ions in the electrolyte and resistance to flow of electrons through the electrodes. The dominant ohmic losses through the electrolyte are reduced by enhancing the ionic conductivity. For the concentration polarization, as a reactant is consumed at the electrode by electrochemical reaction, there is a loss of potential due to the inability of the surrounding material to maintain the initial concentration of the bulk fluid. Several processes may contribute to concentration polarization, for example slow diffusion in the gas phase in the electrode pores, solution/dissolution of reactants and products into and out of electrolyte, or diffusion of reactants and products through the electrolyte to and from the electrochemical reaction sites (Williams, 2002)

2.4 Commercialized Perfluorosulfonic Acid (PFSA) Membranes

The perfluorosulfonic acid (PFSA) membranes such as Nafion® are the key polymer mostly used in portable fuel cell applications. The research areas currently of interest in Nafion® are: (i) the proton transport phenomena within the membrane; (ii) the limitations and drawbacks of the membrane to reach the significant PEMFC performance; and (iii) the modification made to the membrane to increase its performance.

2.4.1 Proton Transport Phenomena

In order to understand the transportation of protons and water in PFSA membranes, qualitative and quantitative modeling studies have been conducted. The microscopic models studied based on statistical mechanics, molecular dynamics and microscopic phenomena were applied to the structure of the membranes. The microstructure of the PFSA membranes proposed in the early 1980s was reported based on the geometry and phenomenology for the water-swelled polymer and the water-diffused coefficient in the membrane pores (Gierke and Hsu, 1982). It was found out that an inverted micellar structure in which the ion-exchange sites were separated from the fluorocarbon backbones, thus, the spherical clusters (pores) connected by short narrow channels are formed. The model was termed as "cluster network model". Based on this model, an average radius and the number of sulfonic acid groups in the ionic spherical cluster are 18 nm and 26, respectively, when the membrane is dry. In the swollen state, the diameter increases to about 4 nm with ~ 70 sulfonic acid groups while each pore is filled with about 1000 water molecules and the connecting channels have a diameter and length of about 1 nm.

Scheme 2.8 Schematic view in PFSA membranes based on (a) cluster network model; (b) random network model
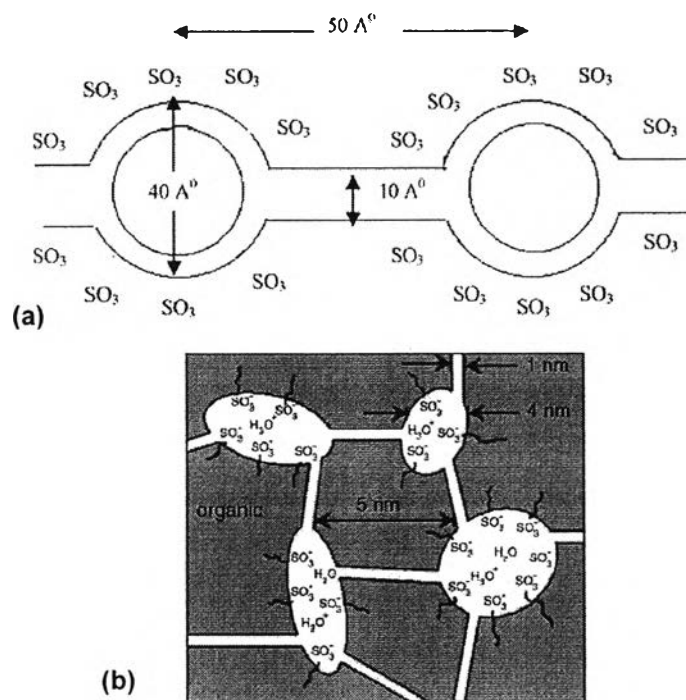
The recent studies named as "random network model", which is a modification of the "cluster network model", was reported based on the percolation properties of the proton conductivity as a function of water content (Eikerling and Kornyshev, 1997). This model includes an intermediate region wherein the side chain ending with pendant sulfonic acid groups tend to be cluster within the overall structure resulting in the formation of hydrated regions. Unlike the "cluster network model", the hydrated regions in this model are distributed randomly in the polymer matrix, which facilitates quicker proton transport upon the rotation of these side chains. In this case, although the hydrated regions drift apart, the transverse motion of protons through the membrane is possible. A schematic draws of the cluster network and random network models are depicted in Scheme 2.8.

2.4.2 Limitations and Drawbacks

From the previous discussion, it is clear that the PFSA membranes are still intensively examined of cell requirements of high proton conductivity,

outstanding chemical stability and longevity of about 60,000 h at 80 °C. However, there are several major drawbacks of these PFSA membranes needed to be overcome as follows

a: Membrane cost. Nafion$^{®}$ membrane and related polymers are expensive, for example amounting approximately of Nafion$^{®}$ 117 membrane in 2007 is for US$ 1944 / m^2 (Gilpa and Hogarth, 2001).

b: Lack of safety during manufacture and use. Safety concerns arise from the evolution of toxic intermediate and corrosive gases liberated at temperature above 150 °C and the decomposed products during the manufacturing processes or vehicle accidents (Ion Power Homepage, 2001).

c: Requirement of supporting equipment. The hydrogen system is added considerable cost and complexity to the vehicle power (Smith *et al.*, 2005).

d: Temperature related limitation. Degradation of PFSA membranes at elevated temperature is another serious drawback. Also, membrane dehydration, reduction in proton conductivity (more than 10 folds), decrease in affinity for water, loss of mechanical strength due to softening of polymer backbone and significant fuel permeation are observed at temperature above 80 °C (Rikukawa and Sanui, 2000).

The use of the membrane at high operating temperature is required in order to improve the PEMFC performance via the increase in oxidative kinetic rate at anode for both hydrogen (PEFC) and methanol (DMFC) as well as the acceleration of proton transferring rate through the membrane (Gosalawit *et al.*, 2006).

e: High fuel and ruthenium (Ru) anodic co-catalyst crossover. All PFSA membranes show the significant high fuel crossover, for example methanol permeability in DMFC with Nafion$^{®}$ membrane is greater than 80,000 barrers at 80 °C (Sakari *et al.*, 1985), which drastically reduces the DMFC performance due to the three reasons: (i) poisoning of cathode catalyst; (ii) fuel efficiency reduction; and (iii) electrode potential reduction because of the methanol oxidation at cathode (Neburchilov *et al.*, 2007). Moreover, the ruthenium (Ru) anodic co-catalyst, which permeates through the membrane and re-deposits on cathode, results in a large decrease in DMFC performance.

2.4.3 <u>Membrane Modifications</u>

Several efforts have been made to improve the performance of Nafion® membranes and to ascertain water retention at higher temperature via incorporating inorganic fillers into Nafion® membrane. Antonucci *et al.* (1999) reported that the composite of Nafion®-silica electrolyte membrane improved the water retention and enabled to operate at temperature above 130 °C. Such membrane could be used in a DMFC at 145 °C with the power density of 240 mW/cm^2. A similar method for water retention in Nafion® membrane at elevated temperature by incorporating silica or titanium oxide into Nafion® polymer matrix for DMFC systems was also reported by Baradie *et al.* (1998). This membrane exhibited significant proton conductivity improvement but did not retard methanol crossover. Also, Shao *et al.* (2004) prepared the composite membrane of Nafion® 115 with silicon oxide doped with phosphotungstic acid for PEMFC. The crystallinity and thermal stability of the composite membrane were improved as well as the same level for proton conductivity with plain Nafion® 115 membrane at high temperature under 100 % relative humidity.

Wasmus *et al.* (2000) improved the performance of DMFC by equilibrating Nafion® 117 membrane with phosphoric acid. The improvement in reaction kinetics accompanied by high proton conductivity up to 200 °C as well as lower methanol crossover compared to Nafion® 117 membrane were achieved. Moreover, a reduction in methanol crossover by coating a thin layer of plasma polymerized tetrafluoroethylene with vinyl phosphoric acid and with chlorosulfonic acid on Nafion® membrane were attempted by Mex and Muller (1999) and Finsterwalder and Hambitzer (2001), respectively.

A significant improvement in proton conductivity at elevated temperature by incorporating perfluorinated ionomers in Nafion® matrix and by doping it with heteropolyacid such as phosphotungstic acid, phosphomolybdenic acid and phosphotin acid was reported by Bahar *et al.* (1996). Tazi and Savadago (2001) also prepared the composite membrane of Nafion® 117 with the incorporation of silicotungstic acid (SA) and with thiophene (TH) in order to enhance the ionic conductivity and power density. The substantial improvement in ionic conductivity was obtained from the membrane of Nafion® 117 incorporated with SA due to the

33 % increase in water uptake as compared to the normal value of 27 % from Nafion® 117 membrane. The highest current density of 810 mA/cm^2 at 600 mV was achieved from Nafion 117 combined with TH while that of Nafion® 117 was 640 mA/cm^2.

2.5 Alternative Membranes for PEMFC Systems

Despite its shortcoming, Nafion® is still the polymeric choice for most PEFC and DMFC applications. However, it is likely that Nafion® will be replaced by an alternative membrane in the future. Rikukawa and Sanui (2000) suggested that in order to produce the material that are less expensive than Nafion®, some sacrifice in material lifetime and mechanical properties may be acceptable, which provides the cost factor to be commercially realistic. However, the uses of hydrocarbon polymers, even though they have low thermal and chemical stability, have attracted renewed interest.

2.5.1 Hydrocarbon Membranes

Hydrocarbon polymers provide some advantages over PFSA polymers, i.e., they are less expensive, commercially available and their structures permits the introduction of polar sites as a pendant group for increasing water uptake. Bryan *et al.* (1999) studied the applicability of pervaporation membrane in DMFCs. Poly(vinyl alcohol) (PVA) membranes are well known as methanol barriers and water soluble polymer; thus, a swelling of PVA could be controlled by crosslink degree. It is important to note that the high water permeability should give high proton conductivity at least when the membranes are equilibrated with phosphoric acid. Besides, Nikolic *et al.* (2007) reported the cross-linked PVA membranes prepared by gamma irradiation. The proton conductivity was measured from the 6 M KOH-impregnated membranes at certain time and temperature. The cross-linked PVA membranes showed the comparable polarization curve to Nafion® membrane as well as the stability during the real cell test.

Hydrocarbon membranes based on polystyrene have also received much attention for fuel cell systems. For example, sulfonated polystyrene (ethylene-

butadiene) polystyrene (SEBS) triblock copolymer was reported by Sangeeth (2005). The membrane revealed excellent conductivity in the order of 10^{-1} S/cm in fully hydrated state at room temperature. Thereafter, Mokrini and Honeault (2006) blended this SEBS with polyvinylidine chloride (PVDF). The SEBS part offer good proton conductivity while PVDF insures good dimensional stability and chemical resistant to the film.

2.5.2 Aromatic Membranes

In order to enhance the thermal, mechanical and chemical stabilities of the membranes at elevated temperature, aromatic hydrocarbons are taken into account. Polyarylenes are high temperature rigid polymers with $T_g > 200$ °C due to the presence of inflexible and bulky aromatic groups (Guth *et al.*, 1999). The aromatic rings offer the possibility of both electrophilic and nucleophelic substitutions. The sulfonation of polyarylenes, e.g., polyethersulfone (PESF) (Kice and Puls, 1977), polyetherketone (PEK) with varying number of ether and ketone functionalities (such as PEEK (Kobayashi *et al.*, 1998), PEKK (Gasa *et al.*, 2007), etc.), poly (arylene ethers) (Hong *et al.*, 2008, Wang *et al.*, 2006), polyester (Zou *et al.*, 2004) and polyimide (Vallejo *et al.*, 1999) are some of the relevant examples for polyaromatic membranes in PEMFC.

There are several studies suggesting that polyester must be avoided since the ester group imparts instability in aqueous acids. The sulfonation of those polyarylenes is controlled by reaction time and temperature. Sulfonated polybenzimidazole exhibited superior performance to Nafion® membrane at high temperature (Bae *et al.*, 2002). Cross-linked polyphosphazenes was also prepared by blending and radiation for the reduction of water swelling and methanol permeation (Carter et al., 2002).

Scheme 2.9 Structures of some polyarylenes used for PEM: (a) sulfonated polysulfone and (b) sulfonated polyether ether ketone

(a)

(b)
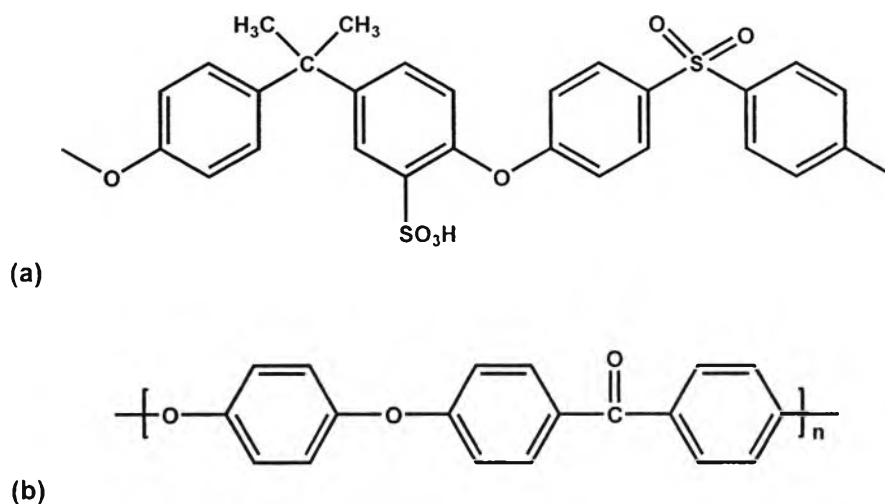
2.5.3 Acid-base Complexes

Acid-base complexes have been considered as one of the alternative membranes which can maintain high proton conductivity at elevated temperature without suffering from dehydration effect. In general, acid-base complexes are considered as an acid component into an alkaline polymer base for proton conductivity. For example, the phosphoric acid (H_3PO_4) doped polybenzimidazole (PBI) showed an independence of proton conductivity with humidity in contrast with Nafion[®] membrane (Qinfeng et al., 2001). These H_3PO_4 doped PBI complexes are sensitive to the doping level and operating temperature, i.e., at the doping level changing from 450 to 1600 % at 165 °C, the proton conductivity increased from about 4.6×10^{-2} S/cm to 0.13 S/cm. A fuel cell was operated with such complexes at 190 °C yielding the power density and current density of 0.55 W/cm^2 and 1.2 A/cm^2, respectively. This might be due to the poison tolerance of the electrode catalyst at elevated temperature is significantly improved (Steiner and Sandor, 1999).

2.5.4 Organic-inorganic Composite Membranes based on Non-perfluorinated Polymer

As mentioned before (section 2.3.3), there have been several attempts based on composite membrane preparation to improve the properties of Nafion[®]

membrane to be able to use at high temperature with low fuel crossover. However, the high cost of Nafion[®] and related polymers is the main drawback for this modification. Therefore, the composite membranes of inorganic fillers with other alternative polymers for a superior propensity to retain water enhance proton conductivity as well improve thermal stability and mechanical robustness and reduce permeability of molecular species (Kumar and Fellner, 2003). Ponce *et al.* (2003) prepared organic-inorganic composite membranes of sulfonated polyether ketone (SPEK) with different heteropolyacids and inorganic framework of ZrO_2 and $RSiO_{3/2}$ for DMFCs. The presence of ZrO_2 decreased methanol and water permeability and the bleeding out of heteropolyacids. Significant conductivity was obtained with the membrane containing tungstophosphoric acid.

In 2007, the varieties of composite membrane preparations with several organic polymer matrices and inorganic contents are investigated. For example, (i) polyvinyl alcohol incorporated with phosphosilicate, the significant proton conductivity of 0.02 S/cm was obtained at ambient temperature under 100 % relative humidity as well as the lower methanol permeation for 5-10 times compared to Nafion[®] 117 was achieved (Jin *et al.*, 2007); and (ii) the composite membrane of sulfonated polystyrene and fullerene, which revealed in the reduction in methanol crossover and 60 % of Nafion-based DMFC performance values (47 mW/cm2 and 200 mA/cm2 for power and current densities, respectively), was reported (Sega *et al.*, 2007).

Among these non-perfluorinated polymers, sulfonated polyether ether ketone (SPEEK) is one of the most promising candidates for composite membrane preparations. In 2000, the composite membranes of SPEEK embedded with heteropolyacids, i.e., tungstophosphoric acid (TPA) and molybdophosphoric acid (MPA) were prepared. The membranes are thermally and mechanically stable up to the temperature above 250 °C as well as the significant proton conductivity of 10^{-2} S/cm at room temperature and of 10^{-1} S/cm at above 100 °C (Zaidi et al., 2000). The incorporation of inorganic fillers such as silicate layers and silica particles into SPEEK polymer matrix was also investigated. Gaowen *et al.* (2005) prepared the exfoliated composite membranes of organic-montmorillonite and SPEEK via solution intercalation technique. The composite membrane revealed significant

methanol crossover reduction as well as approachable proton conductivity to Nafion[®] 115 at 90 °C (1.2×10^{-2} S/cm). Besides, the composite membranes of sulfonic acid functionalized silica and SPEEK prepared by solvent casting was reported by Sambandam and Ramani (2007), which showed the proton conductivity at 80 °C for 0.05 S/cm and 0.01 S/cm under 75 and 50 % relative humidity, respectively. The hydrogen crossover through the membrane was investigated by the oxidation of hydrogen at cathode determined by linear sweep voltammetry. The hydrogen crossover current density for all MEAs was on the order of 1-2 mA/cm^2.

## 2.6 Motivation of the Present Research

2.6.1 Composite Membranes of Krytox-modified Inorganic Fillers and Nafion[®] Polymer

Based on the requirement for the use of the membrane at elelvated temperature (above 100 °C), which provides several benefits, i.e., (i) increase in reaction kinetic rate at both electrodes; (ii) improvement of proton exchange rate; and (iii) CO tolerance for electrocatalyst, the modification of Nafion[®] membrane via organic-inorganic composite membrane with the fillers such as silica particle and clay layered silicate (montmorillonite) is considered. In the previous reports (section 2.3.3), the composite membrane of Nafion[®] with silica doped with phosphotungstic acid reported by Shao et al. (2004) showed the better results for operating at high temperature. Nevertheless, the SEM photographs exhibited the significant organic-inorganic phase separation.

Therefore, we consider the hybrid composite membranes under the concept of "like dissolves like" of Nafion[®]-silica hybrid material for the miscible blend system to obtain the homogeneous composite membrane. The immobilization of silica particles onto the Nafion[®]-liked polymer chains, i.e., Krytox 157 FSL (carboxylic acid terminated perfluoropolyether, Scheme 2.10), which is a type of fluorocarbon polymer, is proposed. The Krytox-modified fillers are accomplished by the using (3-aminopropyl) triethoxy silane as a coupling agent. The organic-inorganic homogeneity of the composite membranes is expected to give the better results for proton conductivity at the wide range of high operating temperature.

Scheme 2.10 Structure of Krytox 157 FSL
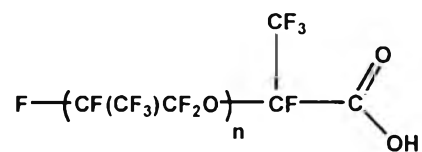
Besides, this modification of Nafion® membrane with inorganic fillers is considered for direct methanol fuel cell (DMFC) systems. Based on the inferior performance of DMFC caused by high methanol crossover through the membrane, the attempts to incorporate inorganic fillers either silica particles or clay layered silicate such as montmorillonite under the concept of "like dissolves like" are also carried out. The methanol crossover reduction is expected to obtain by the tortuousity of the inorganic fillers dispersed in the Nafion® polymer matrix (Scheme 2.11). All properties useful for DMFC usages of the Nafion-based composite membrane will be evaluated as well as the comparative study between this composite membrane (with Krytox-functionalized silica) and hydrocarbon polymer membrane, i.e., sulfonated PEEK-WC (poly(oxa-p-phenylene-3,3-phthalido-p-phenylene-oxy-phenylene) will be considered.

Scheme 2.11 Tortuous pathway of inorganic fillers in the polymer matrix
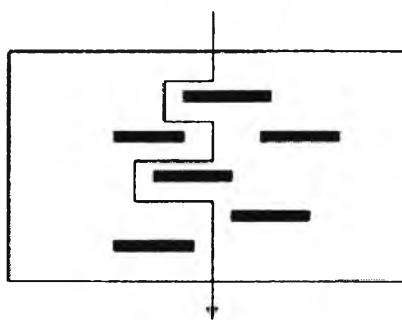
2.6.2 Composite Membrane of Sulfonated Poly(ether ether ketone) (SPEEK) and Sulfonic Acid-functionalized Montmorillonite (SMMT) for DMFCs

According to the high cost of Nafion[®] and its related polymers, the alternative membranes are considered also for composite membrane preparation. Among them, sulfonated poly(ether ether ketone) (SPEEK) is a promising polymer for it good thermal stability and mechanical strength (Li et al., 2007 and Karthikeyan et al., 2005). The proton conductivity of SPEEK depends on sulfonation degree controlled by time and temperature of sulfonation process. Although high proton conductivity is significantly required for the superior fuel cell performance, high methanol crossover through the membrane and the failure in mechanical stability in alcohol environment are the point to be concerned when the degree of sulfonation is increased.

The montmorillonite is considered to be embedded to the SPEEK polymer matrix in order to reduce methanol crossover and improve mechanical stability. However, the incorporation of this silicate layers can cause the inferior proton conductivity; thus, the sulfonic acid functionalization onto montmorillonite layers will be carried out. This composite membrane is expected to reveal the significant DMFC performance as compared to Nafion[®] membrane due to the low methanol crossover, good mechanical stability as well as comparable proton conductivity.