



## CHAPTER I INTRODUCTION

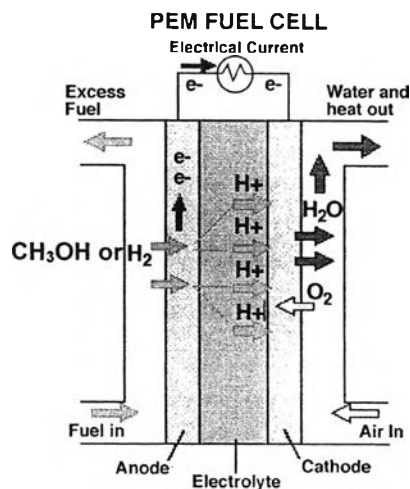
Fuel cell is an electrochemical energy conversion device that converts chemical energy of fuel, e.g. hydrogen, methanol, and oxygen into electricity and heat by electrochemical redox reaction at the electrodes of fuel cell and produces water as the only byproduct. Saving the fossil fuel, due to high efficiency of energy conversion, which is 40-50 % higher than a coal fired power station and an internal combustion engine, renders fuel cell to be preferable as an advanced power system for the future (Sopain *et al.*, 2006). Moreover, fuel cell has received much attention over other energy conversion devices due to its several advantages, for example low pollution level, low noise, low maintenance costs, long operating life, compact design and reliability in used fuels.

Table 1.1 shows briefly the characteristics, advantages and disadvantages of all fuel cell types. There are six types of fuel cells operating in several applications. In general, fuel cells are named and categorized based on their electrolyte and operating temperature. The low temperature fuel cell operating at temperature below 200 °C, i.e., (i) polymer electrolyte fuel cell (PEFC); (ii) direct methanol fuel cell (DMFC), (iii) phosphoric acid fuel cell (PAFC); and (iv) alkaline fuel cell (AFC), while fuel cells operating at high temperature (600-1000 °C) are molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC).

**Table 1.1** Types of fuel cell

<b>Fuel cell</b>	<b>Temperature (°C)</b>	<b>Application</b>	<b>Advantages</b>	<b>Disadvantages</b>
Alkaline Fuel Cell (AFC)	50-90	Space application	High efficiency	Intolerance to CO <sub>2</sub> in impure H <sub>2</sub> and in air, corrosion and expensive
Phosphoric Acid Fuel Cell (PAFC)	175-220	Stand-alone and combined heat power	Tolerance to impure H <sub>2</sub> and commercial	Low power density, corrosion and sulfur poisoning
Molten Carbonate Fuel Cell (MCFC)	600-650	Central, stand-alone and combined heat power	High efficiency and near commercial	Electrolyte instability, corrosion and sulfur poisoning
Solid Oxide Fuel Cell (SOFC)	800-1000	Central, stand-alone and combined heat power	High efficiency and direct fossil fuel	High temperature, thermal stress failure, coking and sulfur poisoning
Polymer Electrolyte Fuel Cell (PEFC)	60-100	Vehicle and portable power	High power density and low temperature	Intolerance to CO in impure H <sub>2</sub> and expensive
Direct Methanol Fuel Cell (DMFC)	50-120	Vehicle and small portable power	No reforming, high power density and low temperature	Low efficiency, methanol crossover and poisonous byproduct

Among them, PEFC and DMFC are two types of fuel cells which use proton exchange membrane (PEM) as a proton exchange part. They have been identified as a promising candidate due to their perceived and simple design, light weight with as-desired compactness and high power density.



**Figure 1.1** Schematic view of PEM fuel cell.

As there are numerous advantages from PEFC and DMFC named as PEM fuel cells (PEMFCs), several researches have focused on these fuel cell systems. One of the most important parts in PEMFC systems is the electrolyte membrane working as a proton exchanging part as well as the barrier for fuel and oxygen. There are several requirements for PEM needed for PEMFCs such as high proton conductivity, mechanical and chemical stability, low fuel crossover and low cost. Nowadays, the lack of suitable PEM still causes the inferior cell performance. A perfluorinated polymer used most extensively produced by DuPont goes by the trade name of Nafion<sup>®</sup>. Similar polymers are Flemion<sup>®</sup> produced by Asahi Glass and Aciplex-S<sup>®</sup> by Asahi chemical (Smitha *et al.*, 2005). Although these perfluorinated membranes especially Nafion<sup>®</sup> membrane provide high proton conductivity, good chemical stability and mechanical strength, they cannot reach the most satisfactory for PEMFCs due to their high methanol crossover and being unable to conduct proton at temperature above 100 °C. The operating system at elevated temperature offers not only the ability to catalytic tolerance of CO in impure hydrogen but also the increase in reaction kinetic rate and acceleration of proton transfer through the membrane.

Due to the drawbacks of Nafion<sup>®</sup> membrane and those requirements for high operating temperature, several attempts have focused on the alternative membranes based on the new synthetic polymer membranes such as the sulfonated polyether ether ketone (SPEEK) (Li *et al.*, 2007), sulfonated polyethersulfone (SPSf)

(Lufrano *et al.*, 2006), polyvinylalcohol (Lin *et al.*, 2005), polyimide (Vallejo *et al.*, 1999) and polyphosphazine (Guo *et al.*, 1999) and organic-inorganic composite membranes with either Nafion<sup>®</sup> or new synthetic polymers as the polymer matrix, for example, Nafion<sup>®</sup>/calcium hydroxyphosphate (Park *et al.*, 2004), sulfonated-silica/Nafion<sup>®</sup> (Yen *et al.*, 2007), SPEEK/nanofillers (Iaponite and MCM41) (Karthikeyan *et al.*, 2005) and SPEEK/ TiO<sub>2</sub> or SiO<sub>2</sub> or ZrO<sub>2</sub> (Nunes *et al.*, 2002).

The present work principally focuses on the composite membranes for PEMFCs either hydrogen fuel cell system (PEFC) or that with methanol aqueous solution (DMFC) to achieve not only the membrane used at elevated temperature ( $T > 100$  °C) but also to decrease the fuel and co-catalyst crossover through the membrane. The strategies for the composite membrane preparation are, i.e., (i) the miscible membrane based on “like dissolves like” concept of Nafion<sup>®</sup> polymer matrix and the inorganic fillers (silica particle and clay layered silicate) modified with Nafion<sup>®</sup>-liked polymer; and (ii) the composite membrane of the fluorine free hydrocarbon ionomers, such as sulfonated poly (ether ether ketone) (SPEEK) with sulfonic acid functionalized inorganic clay (montmorillonite). The filler either silica particle or clay layered silicate initially modified with silane coupling agent to achieve the miscibility between inorganic and organic parts is proposed. The silane-modified filler functionalized with other functional groups, either Nafion<sup>®</sup>-like-polymer chain or sulfonic acid molecule, followed by blending with Nafion<sup>®</sup> or SPEEK solution for further composite membrane preparation is demonstrated. The membrane characterizations covered from chemical structure analyses, physical, thermal and mechanical properties, to the performance related to proton conductivity are carried out to demonstrate how the Nafion<sup>®</sup> and SPEEK are improved.