LITERATURE REVIEW

1. Types of Fuel Cells (Eco Generation Solution LLC. Companies, 2007)

A fuel cell is an electrochemical energy conversion device, similar to a battery in that it provides continuous DC power, which converts the chemical energy from a fuel directly into electricity and heat. The fuel cell produced this energy with clean water as the only byproduct. Fuel cells are classified primarily by the type of electrolyte they employ. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications.

1.1 Phosphoric acid fuel cells (PAFCs)

PAFC used liquid electrolyte in the form of concentrated to 100% orthi-phosphoric acid and platinum as a catalyst. The chemical reactions are shown in Figure 1. These systems operate at temperatures between 150°C and 200°C. This type of fuel cell is typically used for stationary power generation, but some PAFCs have been used to power large vehicles such as city buses. PAFCs are also expensive. Like PEM fuel cells, PAFCs require an expensive platinum catalyst, which raises the cost of the fuel cell.

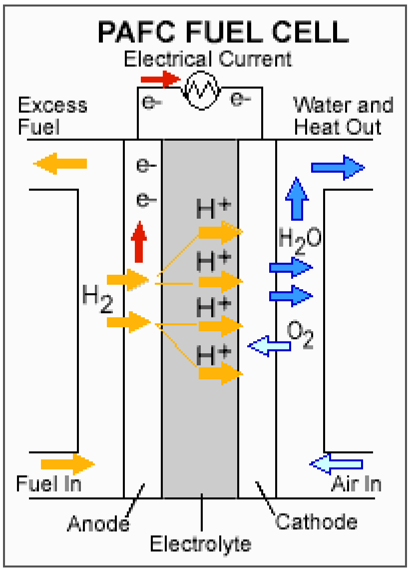

Figure 1 Phosphoric acid fuel cells

1.2 Alkaline fuel cells (AFCs)

AFCs were one of the first fuel cell technologies developed because of their ability to operate over a wide temperature range. AFCs operate at a similar temperature to PEM cells (around 80°C) and therefore start quickly. The electrolyte is potassium hydroxide which is the same chemical Duracell batteries are use and a catalyst is use a variety of non-precious metals at the anode and cathode (Figure 2). This type of fuel cell has been used to provide power and drinking water to space missions, including the US Space Shuttle.

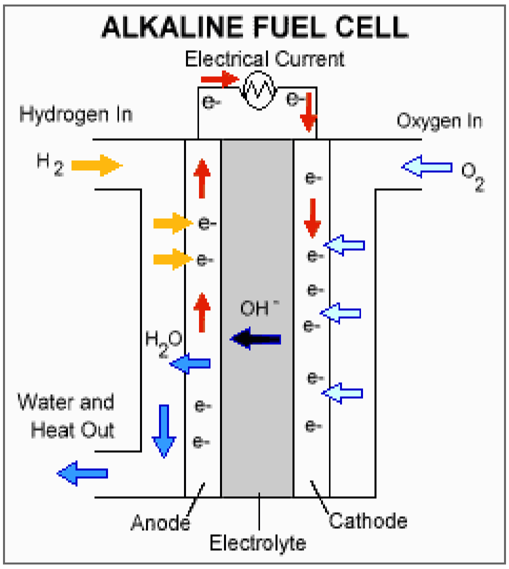

Figure 2 Alkaline fuel cells

1.3 Molten Carbonate Fuel Cells (MCFCs)

MCFCs are currently being developed for natural gas and coal-based power plants for electrical utility, industrial, and military applications. This fuel cell operates at very high temperatures (600-700°C) that allow them to use fuel directly with a simplified fuel processor. The electrolyte was composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide ($LiAlO_2$) matrix (Figure 3).

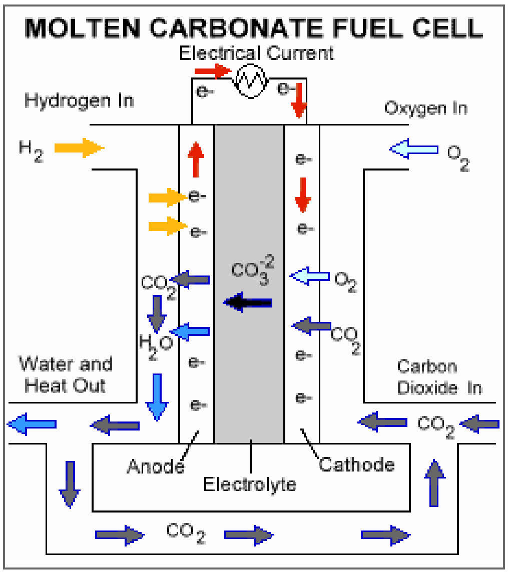

Figure 3 Molten Carbonate Fuel Cells

1.4 Solid oxide fuel cells (SOFCs)

SOFCs use a hard, non-porous ceramic compound as the electrolyte, sandwiched between the anode and the cathode (Figure 4). It runs at a temperature of 1000 °C. The advantages of this system over the tubular system are its relative ease of manufacture and a lower ohmic resistance of electrolyte, resulting in reduced energy losses.

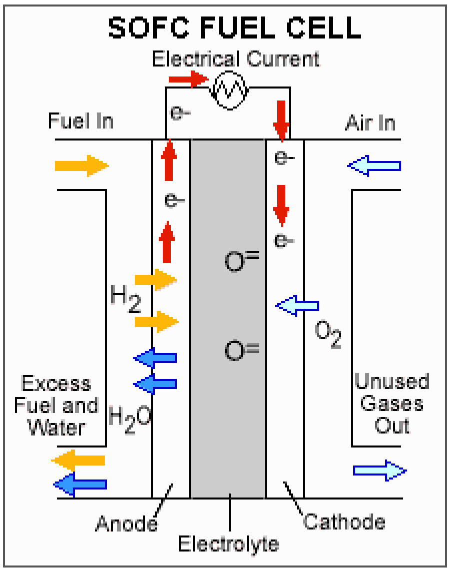

Figure 4 Solid oxide fuel cells

1.5 Direct Methanol Fuel Cells (DMFCs)

This type of fuel cell is based on solid polymer technology but uses methanol directly as a fuel. DMFC utilize a membrane as an electrolyte and produce electricity directly from liquid methanol, eliminating the need for a fuel reformer. Methanol is miscible in water, also some of it is liable to cross the water-saturated membrane and cause corrosion and exhaust gas problems on the cathode side.

1.6 Proton Exchange Membrane Fuel cells (PEMFCs)

PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. PEM fuel cells operate at low temperatures (60-160°C) have high power density, can vary their output quickly to meet shifts in power demand, and are suited for applications where a quick startup is required. As shown in Figure 5.

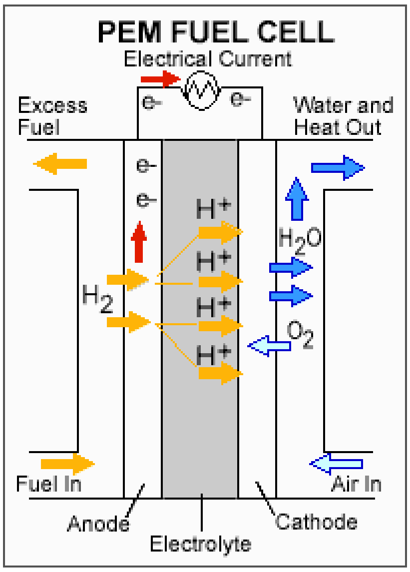

Figure 5 Proton exchange membrane fuel cells

2. Polymer membrane for fuel cells

The typical membrane employed for the PEMFC is sulfonated fluoropolymer, such as fluoroethylene or Nafion (Figure 6). Nafion has popularly been used in PEMFC because of its excellent chemical, physical and electrical properties.

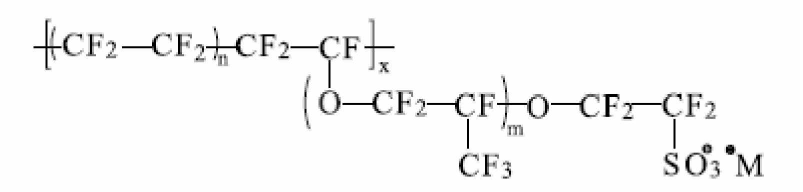

Figure 6 The structure of Nafion

The proton conductivity of Nafion is on the order of 0.083 s/cm at 100 % relative humidity and 25°C (DuPont, 2004). However, some disadvantages of Nafion for PEMFC applications have become apparent: its too expensive price and its unstable thermal stability at high temperature. As a result, several new membrane structures have been studied by various research groups. Gil (Gil *et al.*, 2004)and Jiang (Jiang, 2005) sulfonated the poly (ether ether ketone) (SPEEK). The SPEEK membrane showed the proton conductivity increment with degree of sulfonation, relative humidity and temperature. The highest conductivity was 0.070 s/cm at 25°C and 100 % relative humidity. In addition, the ion exchange capacity (IEC) was obtained 1.5 meq/g. The sulfonated of poly (arylene ether sulfone)s done by Xixo (Xiao *et al.*, 2002) had high ion exchange capacity (IEC) on the order of 1.71 meq/g and T_g of 317°C, very stable at high temperature. Due to its comparable proton conductivity to that of Nafion, poly (arylene ether sulfone) has potential to be used as PEMFC membranes.

Mecham (Mecham, 2001) reported about more advantages of the direct condensation copolymerization than conventional post-sulfonation of poly (arylene ether sulfone) such as better defined location and ion conductor concentration, improved stability, the ability to produce much higher molecular weights than available commercial-based systems, and rather higher acidity which was due to the influence of the sulfonic acid groups being attached to meta-positions of deactivated sulfonyl groups instead of the ortho-positions of activated rings having ether bonds as in the case of the post sulfonation reaction. Furthermore, precise control of sulfonation with two sulfonic acid groups per repeating unit could be achieved. Indeed, the acid form of these membranes showed good thermal stability by thermogravimetric analysis (TGA) (>220˚C in air). The fully hydrated acidic membranes had proton conductivites of 0.11 and 0.17 s/cm for the 40 and 60 mol% disulfonated copolymers in liquid water at 30˚C, respectively, which were comparable to or higher than that of Nafion 1100 at the same condition.

In recent years, organic-inorganic composites have been investigated for PEMFCs with only one major purpose, which is to increase proton conductivity of membranes. Yang (Yang *et al.*, 2004) illustrated that the inclusion of zirconium phosphate into Nafion membranes exhibited good cell performances at 130°C because zirconium phosphate can keep the water within the membrane at high operating temperature. Kwak (Kwak *et al.*, 2004) prepared composite membranes by adding the mordenite into the Nafion and found that at high temperature above 90°C the proton conductivity of the composite membranes increased with increasing mordenite content. Kim (Kim *et al.*, 2004) obtained the composite membranes by mixing sulfonated organic polymer with inorganic material, SiO_2, using the sol-gel process. Due to its higher water uptake and thermal stability of composite membranes, the cell performance at high temperatures above 100°C was improved. In addition, the SiOH group in a composite membrane was shown to play a major role in capturing water strongly and maintaining proton conductivity at high temperature. But the tensile strength decreased as the silica content was increased. Baglio (Baglio *et al.*, 2005) prepared the composite membrane by adding the chabazite and clinoptilolite into the Nafion. These composite membranes showed the cell performance (around 350–370 $mWcm^{-2}$ under oxygen feed, 200–210 $mWcm^{-2}$ under air feed, at 140°C) better than that with nafion 117 at the similar condition. That's because zeolites can help to maintain the water in the cell at higher temperature.

Zeolite has a three-dimensional network composed of interconnected (Si, Al)O_4 tetrahedra. The cations are linked with the framework by water molecule (Figure 7). There are several of different zeolites found in nature and made by man. That's depends upon the exact shape, size, and charge distribution of the lattice structure of the zeolite (Figure 8). Zeolites with low Si/Al ratios have strongly polar anionic frameworks. The exchangeable cations create strong local electrostatic fields and interact with highly polar molecules such as water. Thus, the zeolite helps to capture water strongly to maintain proton conductivity at high tempertature.

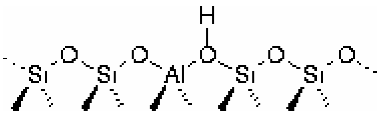

Figure 7 The structure of zeolite was framework by water molecule

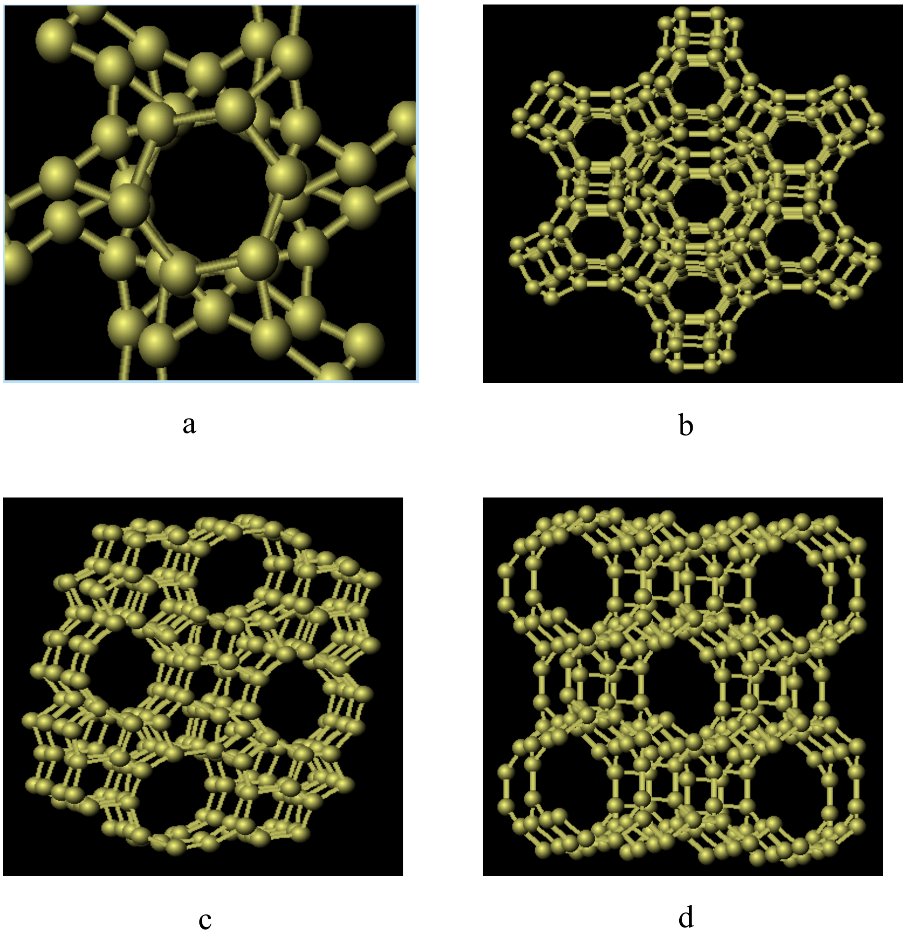

Figure 8 The structure of zeolite a) Analcime b) Zeolite Y c) ZSM-5 d) Mordernite

ZSM-5 can easily be produced from local materials, such as rice husk, and thus its price is lower than other zeolites.(Lohsoontorn, 2006)

Recently, heteropolyacids (HPAs) (Zhang *et al.*, 2006) are one of the most attractive inorganic modifiers because these inorganic materials in crystalline form have been demonstrated to be highly conductive and thermal stable. HPAs, such as phosphotungstic acid (PTA), silicotungstic acid (STA), phosphomolybdic acid (PMA), and silicomolybdic acid (SMA), are known to have different hydrated structures depending on environments. HPA in dehydrated phase, or in a polar solvent, has the so-called primary structure, which is also called a Keggin unit (Figure 9). The Keggin unit consists of a central atom in a tetrahedral arrangement of oxygen atoms surrounded by 12 oxygen octahedra connected with tungsten or molybdenum.

There are four types of oxygen atoms found in the Keggin unit; the central oxygen atoms, two types of bridging oxygen atoms, and the terminal oxygen atoms. (Fenton *et al.*, 2004) Kreuer suggested the HPA acts as a Bronsted acid toward the water of hydration, which is generally loosely bound in the structure, resulting in high proton conductivity. Similar to Figure 8, Figure 9 shows the Kegging unit of PTA.

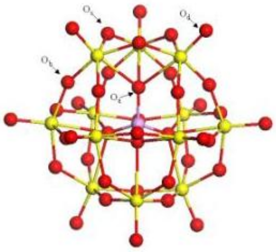

Figure 9 The primary structure of Keggin unit

Zhang (Zhang *et al.*, 2005) and Ponce (Ponce *et al.*, 2004) prepared phosphotungstic acid/sulfonated poly(arylene ether nitriles ketone) composite membranes which showed lower water sorption but higher proton conductivity. Kim (Kim *et al.*, 2003) described the preparation of phosphotungstic acid/sulfonated poly (arylene ether sulfone) composite membranes with different disulfonation levels of the polymer matrix via solution blending. The composite membrane not only had good thermal stability, but showed enhanced mechanical strength and lower water uptake than the unfilled membranes. The proton conductivity of the well dispersed HPA incorporated sulfonated copolymer system has been quite promising at temperatures greater than the boiling point of water owing to the specific interactions between HPAs and sulfonated copolymers, which is not yet well understood.