

2.0 INTRODUCTION AND BACKGROUND

The advance made in science and technology has contributed immensely to continued industrial growth and development. Such development is critical for the future as it leads to progress and improvement of the quality of life. However it can also cause serious environmental deterioration if not carefully controlled, introducing foreign materials into and polluting the atmosphere (Odigure, 1999; Silva, 2005). Pollution is a by-product of human activities originating in primitive agricultural farming techniques and continuing into today's high technology industrial activities. Industrialisation is highly desirable for the sustenance of a nation economy and enhancement of its citizenry's well being. However the negative impact, precipitated by the introduction of its unwanted by-products into ecological systems, may be catastrophic if allowed to build up uncontrolled. Hence there is the need to consider the environmental impact during the design, development and operation of process industries. It has been reported that the natural systems, i.e. atmospheric, land and sea as well as lives of plants, are clearly being disturbed because of the complete reliance on the combustion of fossil fuels as a source of energy for power generation in the industries and for the running of vehicles (Odigure et al, 2005; Hussain et al, 2005). In addition to the health and environmental concerns resulting from this complete dependence on fossil fuel as a source of energy, a steady depletion of the world's limited fossil fuel reservoir is also demanding the exploration and development of new energy technologies for energy conversion and power generation. The new energy conversion technology should be more efficient than the conventional heat engine, with minimal or no pollutant emissions, and also compatible with renewable energy sources for sustainable development (Marr and Li, 1998; Xianguo, 2006; Inoue et al, 2006). The transition experienced by the global energy source in the mid-19th century from wood to hay to coal, and nuclear to oil and

hydrocarbon and then to natural gas, shows the tendency of the global energy shift from solid to liquid and from liquid to gases, and most recently to non polluting energy sources (Bai et al, 2006). These transitions are in line with the prediction of energy sources as a tool for sustainable economic growth, based on the belief that a time will be reached when the demand for non- polluting and efficient energy sources will be met globally by sources other than fossil fuel (Cheddie and Munroe, 2005). Recent contributions to the literature reveal that we have now reached the age of non polluting energy sources. Internationally the challenge is to produce non polluting energy sources, and fuel cells are expected to play a major role in achieving such objectives (Yi and Nguyen, 1999; Smitha et al, 2005; Souzy et al, 2005; Bai et al, 2006; Ha et al, 2006).

Fuel cells have been identified as one of the most promising and potential clean energy technologies which meet all the requirements for energy security, economic growth and environmental sustainability, and have attracted considerable attention as a possible replacement for power generation systems (Appleby, 1992; Klaiber, 1996; Wang et al, 2005;; Li et al, 2005; Shang et al, 2005; Li et al, 2005). They were described by Schlake et al (2006) as the perfect melding of benefits from energy sources, the result of their ability to emulate the ease of refueling and continuous operation potential from internal combustion engines, as well as the highly efficient and quiet operation of batteries: Fuel cells thus appear to be an ideal energy alternative (Ying et al, 2005; Haraldsson and Alvfors, 2005; Oedegaard and Hentschel, 2006). They lack the need for recharging that batteries have and also the pollution creation that plagues both batteries and combustion engines (Lee et al, 2002; Ying et al, 2005; Chen et al, 2006; Bischoff, 2006; Thomassin et al, 2006). Fuel cells generate electricity directly from fuel by way of an electrochemical reaction, which is an efficient process (Lamyi et al, 2004; Kundu et al, 2005; Karimi et al, 2005; Chen et al, 2006). Because fuel cells create electricity in this

simple manner, they can be used in a myriad of different ways and have been deployed among electricity consumers as a strategy to their substantial market penetration (Millet and Mahadevan, 2005; Shuo et al, 2005; Shibasaki et al, 2005). When combustion engines generate power, a large portion of the energy of combustion is lost to waste heat and friction, resulting in their low efficiency. The lack of friction within a fuel cell, coupled with the lack of moving parts, contributes greatly to the low maintenance required by fuel cells (Kundu et al, 2005; Kjeang et al, 2006). Other byproducts of combustion include pollutants such as sulphur dioxide and nitrogen oxides (Odigure et al, 2003; Hussain et al., 2005). Fuel cells, again because of their particular mechanism of operation, produce minimal or no pollutants, depend on the type of fuel cell (Kulikovsky, 2003; Chen et al, 2005). The United State Department of Energy (DOE) projected that if 10% of automobiles used in the United State were powered by fuel cells, air pollutants would be cut by one million tons per year and 60 million tons of carbon dioxide would be eliminated from the yearly greenhouse gas production. The DOE has also stated that advanced fuel cells using natural gas could potentially reduce carbon dioxide emissions by 60% compared to a conventional coal plant, and by 25% compared to today's natural gas plants (Millet and Mahadevan, 2005). In fact, fuel cells running on hydrogen derived from a renewable source would emit nothing more than gaseous water (Cheddie and Muroe, 2005). Another benefit of the use of fuel cells, making it similar to some industrial combustion processes and better than others, is the ability to capture excess heat generated for use in a cogeneration-like manner or for space/water heating (Matelli and Bazzo, 2005; Zhang et al, 2005; Coutelieris et al, 2005; Assabumrungrat et al, 2005). These methods of increasing the overall efficiency of the fuel cell have been shown to push the efficiency to approximately 80% for both phosphoric acid and molten carbonate fuel cells (Ghouse et al, 1998). Like combustion engines, fuel cells operate using fuel

from tanks that can be easily refueled as long as fuel is fed, and the cell can run continuously. The major advantages that fuel cells hold over internal combustion engines, however, are high efficiency of operation and lack of harmful pollutants (Mattelli and Bazzo, 2005; El-Sharkh et al, 2006).

Fuel cells face many obstacles which researchers and industries must overcome before they can be widely introduced into the marketplace (Woo et al, 2003; Jung et al, 2004; Paturzo et al, 2005; Saarinen et al, 2005; Silva et al, 2005; Choi et al, 2006). There is, however, substantial motivation to solve these problems because fuel cells offer several advantages over other methods of power production. Interest in research and development in fuel cell technology is as a result increasing rapidly, and it should be noted that governments, universities and companies are all gradually adapting to the technology of fuel cells (Kjeang et al, 2006). In addition, it can be noted that fuel cells have been successfully delivering power to several prototypes and specialized applications in recent decades (Hikita et al, 2001; Lee et al, 2002; Schumacher et al, 2004). The power output of a fuel cell stack is easily scalable to provide the right amount of electricity for a laptop computer, a small car, a city bus, or even utility generation and power building not connected to a national grid (Ge and Liu, 2005; Nitsche et al, 2005; Lawrence and Boltze, 2006). The designer simply has to select the right type of fuel cell for the application. Consequently, commercial fuel cell stacks are already becoming available in the market; consumers today can buy a lightweight 1200 watt fuel cell stack from Ballard Power Systems, enabling them to produce electricity wherever there is a source of hydrogen. Although fuel cells technologies are not the purest alternative clean energy (because the technology of fuels on which they depend are produced via a process that may not be environmental friendly) they nonetheless allow the emission

points of pollution to be pushed further back in the chain where they can be more easily collected and dealt with.

Surprisingly, fuel cells are often regarded as representing a technology of the future in their capacity for sustainable power generation; in reality they are one of the oldest energy conversion devices (Xianguo, 2006; Choi et al, 2006). They have not been fully commercialized in several decades of their recognition due mainly to the high cost of their development and application for practical purposes (Schultz and Sundmacher, 2005; Dhar 2005). This has resulted in the perception of fuel cell development as lagging behind when compared with the competitive technologies of heat engines, such as the steam and internal combustion engines. In order to achieve the commercialization of fuel cell technology, especially Proton Exchange Membrane Fuel Cell (PEMFC), there is a need to reduce the cost of the membrane and other components of the fuel cell, as well as the monopolization of membrane synthesis technologies by only a few companies and nations. Relevant literature reveals that during the last decades a cost reduction of ten percent has been achieved; but more research is needed to reduce the cost of a fuel cells system to a competitive level. This could be achieved by cost reduction in all aspects of fuel cells production, material systems and application, together with those of related components (Choi et al, 2006). With regard to the commercialization of fuel cells, the utilization of the locally available material (i.e. polystyrene butadiene rubber) in the synthesis of the membrane and its grafting with carbon nanoparticles so as to improve its qualities in terms of proton conductivity, thermal stability, solvent uptake, porosity to solvent and fuel crossover will contribute to the reduction in the cost of fuel cell production and the improvement of its efficiency. This will have the desired result of finding more applications for fuel cell technology, and is the focus of this current research.

2.1 General Fuel Cell Concepts

A fuel cell is a device that generates electricity directly from a chemical reaction. It has been described as the chemical engineering method of producing energy through electrochemical redox reactions which take place at the cathode and anode of the cell (Kundu et al, 2005; Matelli and Bazzo, 2005; Coutelieris et al, 2005; Promislow and Wetton, 2005; Sopian and Wan Daud, 2006). The fuel cell offers the promise of a low-polluting and highly efficient energy source which can be designed to utilize an almost limitless abundance of fuel (Woo et al, 2003; Jung et al, 2004; El-Sharkh et al, 2006). Unlike the battery, it is designed for the continuous replenishment of the reactant consumed, and produces electricity from an external supply of fuel and oxygen as shown in Figure 2.1 (Iyuke et al, 2003). Every fuel cell has two electrodes and an electrolyte. The two electrodes are positive and negative, called the cathode and anode respectively. They allow the reactions that produce electricity, while the electrolyte plays a key role of permitting only the appropriate ions to pass between the anode and cathode (Iyuke et al, 2003; Biyikoglu, 2005). If free electrons or other substances could travel through the electrolyte, they would disrupt the chemical reaction, and the catalyst function, which speeds the reactions at the electrodes (Larminie and Dicks, 2001). One great appeal of fuel cells is that they generate electricity with very little pollution; hence the fuel cell has become the leading candidate to replace the internal combustion engine and other lower energy density power storage devices such as batteries. Much of the hydrogen from the fuel and oxygen used in generating electricity ultimately combines to form a harmless by-product, namely water. The purpose of a fuel cell is to produce an electrical current that can be directed outside the cell to do work, from powering an electric motor to illuminating a light bulb. A fuel cell generates electricity chemically, rather than by combustion, and is hence not subject to the thermodynamic laws that limit a

conventional power plant. Therefore, fuel cells are more efficient in extracting energy from a fuel. Waste heat from some cells can also be harnessed, boosting system efficiency still further. Because of the way electricity behaves, the current generated by a fuel cell returns to the cell, completing an electrical circuit. Therefore, the chemical reactions that produce this current are the key to how a fuel cell works.

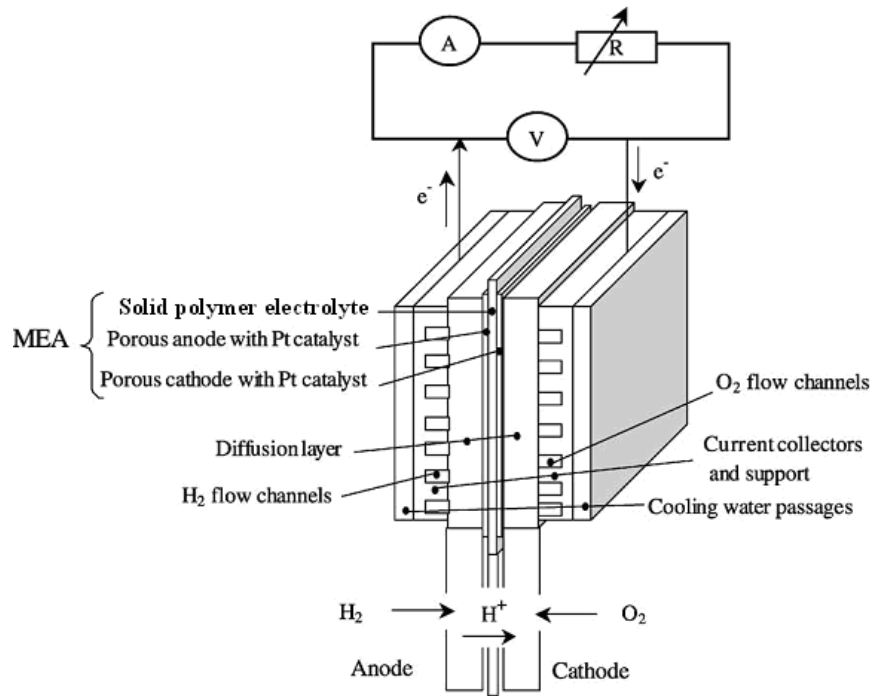


Figure 2.1: Basic Fuel Cell Components (Iyuke et al., 2003)

2.1.1 Types of fuel cells

Proton exchange membrane, solid oxide, alkali, molten carbonate and phosphoric acid fuel cells are the five types of fuel cells currently available in the market. The first two are solid electrolyte while the last three are liquid electrolyte. The type of electrolyte in each fuel cell determines the type of fuel used in each. Some of them require pure hydrogen and therefore need reformer to purify the fuel, while some can tolerate impurities, although they require a high temperature to operate effectively. All five types

of fuel cells have their merits and drawbacks; however none is commercially available at a cheaper price to compete with the existing energy source. Below are the descriptions of different types of fuel cells, classified according to type of electrolyte employed in generating electricity. Each operates slightly differently, as shown in Table 2.1 (Sopian and Wan Daud, 2006). However, in general terms, hydrogen atoms enter a fuel cell at the anode where a chemical reaction strips them of their electrons. The hydrogen atoms are now ionized, and carry a positive electrical charge. The negatively charged electrons provide the current through wires to do work. If Alternating Current (AC) is needed, the Direct Current (DC) output of the fuel cell must be routed through a conversion device called an inverter.

Table 2.1: Overview of Fuel Cells

Fuel Cell	Electrolyte	Operating Temperature (°C)	Electrochemical Reactions
Polymer Electrolyte Membrane (PEMFC)	Solid organic polymer	30-80	$\text{Anode: } H_2 \rightarrow 2H^+ + 2e^-$ $\text{Cathode: } \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ $\text{Cell: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Solid Oxide (SOFC)	Solid zirconium oxide	600-1000	$\text{Anode: } H_2 + O^{2-} \rightarrow H_2O + 2e^-$ $\text{Cathode: } \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$ $\text{Cell: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	175-200	$\text{Anode: } H_2 \rightarrow 2H^+ + 2e^-$ $\text{Cathode: } \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ $\text{Cell: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100	$\text{Anode: } H_2 + 2(OH^-) \rightarrow 2H_2O + 2e^-$ $\text{Cathode: } \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$ $\text{Cell: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Molten Carbonate (MCFC)	Solution of lithium, sodium and/or potassium carbonates soaked in a matrix	600-1000	$\text{Anode: } H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ $\text{Cathode: } \frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ $\text{Cell: } H_2 + \frac{1}{2}O_2 + CO_2 \rightarrow H_2O + CO_2$ Since CO₂ is consumed at anode and produced at cathode, it is therefore included in each side of the equation

2.1.1.1 Alkali fuel cell

Alkaline fuel cells (AFC) are interesting alternatives to polymer electrolyte membrane fuel cells (Gulzow et al, 2006). They operate on compressed hydrogen and oxygen. They generally use a solution of potassium hydroxide in water as their electrolyte. The

hydroxyl ion (OH^-) from potassium hydroxide migrates from the cathode to the anode. At the anode, hydrogen gas reacts with the OH^- ions to produce water and release electrons. Electrons generated at the anode supply electrical power to an external circuit, then return to the cathode. There the electrons react with oxygen and water to produce more hydroxyl ions that diffuse into the electrolyte. Its efficiency is about 70 percent, and the operating temperature is 90 to 100°C (Crawley, 2006; Tewari et al, 2006). The cell output of AFCs ranges from 0.3kW to 5kW and like other fuel cells, creates little pollution (Crawley, 2006; Lin et al, 2006 and Tewari et al, 2006). Because they produce potable water in addition to electricity, they have been a logical choice for spacecraft. A major drawback, however, is that alkali cells need very pure hydrogen; otherwise, an unwanted chemical reaction forms a solid carbonate that interferes with the other chemical reactions inside the cell (Matsuoka et al, 2005; Varcoe and Slade, 2006; Tewari et al, 2006). Since most methods of generating hydrogen from other fuels produce some carbon dioxide, the need for pure hydrogen has slowed work on alkali fuel cells in recent years (Tewari et al, 2006; Crawley, 2006). Another drawback is the need for large amounts of a costly platinum catalyst to speed up the reaction.

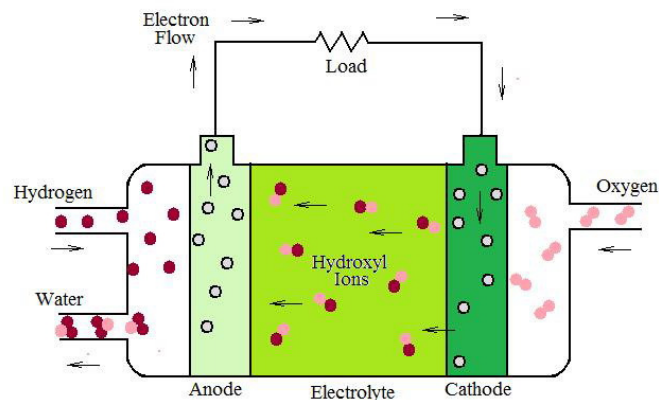


Figure 2.2: Alkali fuel cell (AFC)

NASA selected alkali fuel cells for the Space Shuttle fleet, as well as the Apollo program, mainly because of power generating efficiencies that approach 70 percent (Lin et al, 2006; Crawley, 2006). Alkali cells also provide drinking water for the astronauts. The cells are expensive: the platinum electrode catalyst perhaps makes this fuel type too expensive for commercial application and, like any other container filled with liquid, these fuel cells can leak. Several companies are nevertheless examining ways to reduce costs and improve the cells' versatility (Gulzow et al., 2006; Crawley, 2006). Most of the alkali fuel cells are being designed for transport applications.

2.1.1.2 Molten carbonate fuel cell

Molten Carbonate Fuel Cell (MCFC), presented in Figure 2.3, requires a high-temperature compound of salt like sodium or magnesium carbonates as the electrolyte (Brouwer et al, 2005; Alkaner and Zhou, 2006). Its efficiency ranges from 60 to 80 percent, and the operating temperature is about 650°C (Hishinuwa and Kunitaka, 2004; He, 1997; Yoshida et al, 2004; Kim et al, 2004; Brouwer et al., 2005; Oh and Kim, 2005; Wee, 2005; Hong et al, 2006). The power output from MCFC is up to 2MW (Amorelli et al, 2004; Youn et al, 2006; Bischoff, 2006). The high operating temperature of the cell limits damage from the carbon monoxide poisoning of the cell and waste heat can also be recycled to make additional electricity (Amorelli et al, 2004; Brouwer et al, 2005). Their nickel electrode-catalysts are inexpensive compared to the platinum used in other cells but the high operating temperature also limits the materials and safety uses of MCFCs, making it too hot for home use. A major difficulty with molten carbonate technology is the complexity of working with a liquid electrolyte rather than a solid (Kim et al, 2004; Youn et al, 2005). Another stems from the chemical reaction inside a molten carbonate cell. Carbonate ions from the electrolyte are used up in the reactions at the anode,

making it necessary to compensate by injecting carbon dioxide at the cathode (Amorelli et al, 2004; Youn et al, 2005). In a MCFC, the electrolytes (salt of sodium or magnesium carbonate) are heated to 650°C , and the salts melt and conduct carbonate ions (CO_3^{2-}) from the cathode to the anode. At the anode, hydrogen reacts with the ions to produce water, carbon dioxide, and electrons (Brouwer et al, 2005; Hong et al, 2006; Bischoff, 2006). The electrons travel through an external circuit, providing electrical power along the way. They then return to the cathode, where the oxygen from the air and carbon dioxide recycled from the anode react with the electrons to form CO_3^{2-} that replenishes the electrolyte and transfers current through the fuel cell. Demands for MCFC are limited to large stationary power plants because of its high operating temperature (Grotsch et al, 2006). The high operating temperature of the cells allows the opportunity of using its by-product waste heat to make steam for space heating, industrial processing and a steam turbine capable of generating more electricity (Bischoff, 2006; Krumbek et al, 2006).

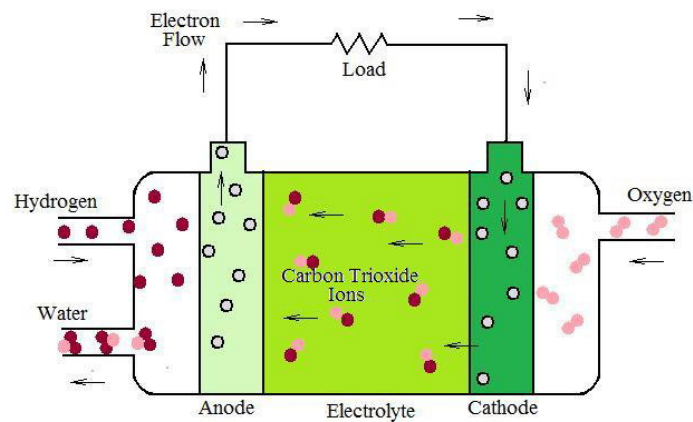


Figure 2.3: Molten Carbonate Fuel Cell (MCFC)

2.1.1.3 Phosphoric acid fuel cell

The energy crises of the 1970s inspired researchers at Los Alamos National Laboratory to begin studying fuel cells (Sammes et al, 2004). Their objective being to develop electric vehicles, they were able to design a golf cart powered by a phosphoric acid fuel cell. Phosphoric Acid Fuel Cells (PAFCs) currently available require a warm-up period, a fact that has limited their use in private cars (Hojo et al, 1996; Choudhury et al, 2002). The efficiency rate of Phosphoric Acid Fuel Cells (PAFCs) averages between 40 to 50 percent, but if the waste heat is reused in a cogeneration system its efficiency can rise to 80 percent (Ghouse et al, 1998; Sammes et al, 2004; Bizzari and Morini, 2004). Existing PAFCs of up to 200 kW capacities are in commercial operation, and units of 11 MW capacities have been tested (Neergat and Shukla, 2001; Kwak et al, 2004).

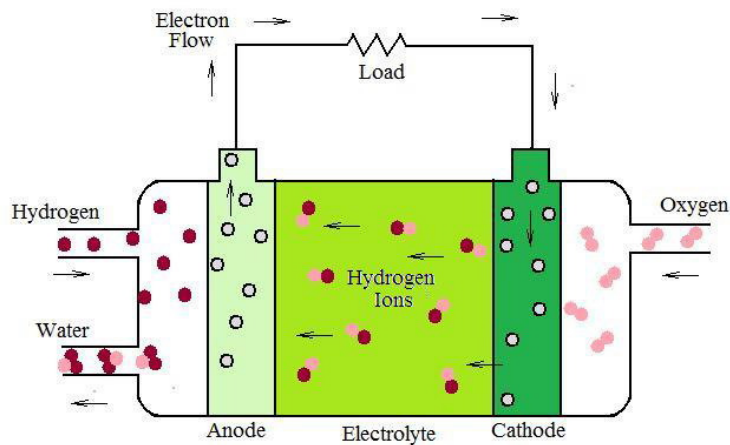


Figure 2.4: Phosphoric Acid Fuel Cell (PAFC)

Phosphoric Acid Fuel Cells (PAFCs) operate at temperatures around 150 to 200°C, and use phosphoric acid as the electrolyte, while a platinum catalyst at the electrodes speeds the reactions (Choudhury et al, 2001; Kwak et al, 2004; Zervas et al, 2006). Positively charged hydrogen ions migrate through the electrolyte from the anode to the cathode.

Electrons generated at the anode travel through an external circuit, providing electric power along the way, and returning to the cathode. At the cathode, the electrons, hydrogen ions and oxygen form water (Choudhury et al, 2005). PAFCs tolerate a carbon monoxide concentration of about 1.5 percent, which broadens the choice of fuels they can use (Jalani et al, 2006). If gasoline is used, the sulfur must be removed. Platinum electrode-catalysts are needed, and internal parts must be able to withstand the corrosive acid (Sammes et al, 2004).

2.1.1.4 Solid oxide fuel cell

Solid Oxide Fuel Cells (SOFCs) are best suited for large-scale stationary power generators that are able to provide electricity for factories and towns (Fergus, 2006; Tremblay et al, 2006; Lee et al., 2006; Zhan and Barnett, 2006). SOFCs shown in Figure 2.5 use a hard ceramic compound of metal such as calcium oxide or zirconium oxide as the electrolyte, though other oxide combinations have also been used as electrolytes (Lin and Beale, 2006; Zhan et al, 2006; Ishiara et al, 2006). The solid electrolyte is coated on both sides with specialized porous electrode materials. The cell efficiency is about 60 %, and operating temperatures are about 1000°C. The high operating temperatures allow the SOFCs to co-generate waste heat and to generate steam for space heating, industrial processing, or in a steam turbine, to make more electricity (An et al, 2006; Lin and Beale, 2006; Ge et al., 2006; Jurado, 2006; Muccillo, 2006; Besra et al., 2006; Jamsak et al, 2006; Jurado, 2006; Xie et al, 2006). At these high temperatures, oxygen ions (with a negative charge) migrate through the crystal lattice. When a fuel gas containing hydrogen is passed over the anode, a flow of negatively charged oxygen ions moves across the electrolyte to oxidize the fuel (Muccillo, 2006; Reitz and Xie et al, 2006; Zhu et al, 2006). The oxygen is supplied, usually from air, at the cathode. Electrons generated at the anode travel through an external load to the cathode, completing the circuit and

supplying electric power along the way. SOFCs output is up to 100 kW and because of the high operating temperatures a reformer is not required to extract hydrogen from the fuel, and waste heat can be recycled to make additional electricity (Jurado, 2006). However, the high temperature limits applications of SOFCs units and they tend to be rather large; while solid electrolytes cannot leak, they can crack (Ge et al, 2006; Sanchez, 2006).

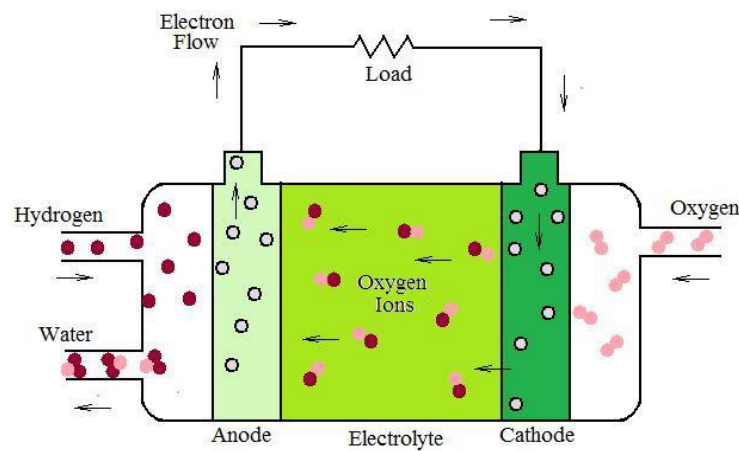


Figure 2.5: Solid Oxide Fuel Cell (SOFC)

2.1.1.5 Proton exchange membrane fuel cell

Since the mid-1980s, Polymer Electrolyte Membrane Fuel Cells' (PEMFCs) development has included stationary power applications (Oedegaard and Hentschel, 2006; Cleghorn et al, 2006). In 1989, Ballard Systems introduced a 5 kW hydrogen and air PEM stack. Two years later, GPU and Ballard introduced a 250 kW plant at Crane Naval Air Station in Indiana. 5kW Plug Power's PEM unit in Albany, New York, intended for home use and demonstrated in June 1998, was the most publicized of PEMFCs available. The 5kW power plant helped the company to make significant

partnerships with both GE and Detroit Edison. These partnerships had hoped to market a residential fuel cell during 2002; however those plans have been postponed.

PEMFCs are one of the most promising fuel cell types for widespread use (Lee et al, 2002). They are exceptionally responsive to varying loads and increasingly cheap to manufacture (Jung et al, 2004; Bettelheim et al, 2004). The PEM fuel cell uses an advanced plastic electrolyte in the form of thin permeable sheet to exchange protons from the anode to the cathode (Kim et al, 2006). The PEMFCs solid electrolyte is much easier to handle and use than a liquid counterpart, and its low operating temperature allows a quick start up (Wang et al, 2006; Song et al, 2005). To speed the reaction, a platinum catalyst is used on both sides of the membrane. PEMFCs efficiency is about 40 to 50 percent, and the operating temperature is about 80°C (Dohle and Stolten, 2002; Shukla et al, 2002). Cell outputs generally range from 50 to 250 kW. The solid, flexible electrolyte will not leak or crack and these cells operate at a low enough temperature to make them suitable for homes and cars (Hikita et al, 2001). In PEMFCs, hydrogen atoms from the fuel sources are stripped of their electrons at the anode, and the positively charged protons diffuse through one side of the porous membrane and migrate toward the cathode. The electrons pass from the anode to the cathode through an exterior circuit and provide electric power along the way. At the cathode, the electrons, hydrogen protons and oxygen from the air combine to form water. For this fuel cell to work, the proton exchange membrane electrolyte must allow hydrogen protons to pass through, but prohibit the passage of electrons and heavier gases.

There are two types of proton exchange membrane fuel cells, i.e., Hydrogen Fuel Cells and Direct Methanol Fuel Cells (DMFC), both of which utilize Proton Exchange Membrane (PEM) to transfers protons (Xu et al, 2005; Shimazaki et al, 2006). High

power fuel cell and high performance favour the choice of Hydrogen Fuel (Rousseau et al, 2006). Also, hydrogen powered fuel cells are the greenest fuel cells, producing only water as a by-product (Kordesch, 1971). However, lack of storage and distribution infrastructures militate against the use of hydrogen. As a result, containment and distribution problems need to be solved before hydrogen fuel can be used on a large scale for commercial purposes. The main advantage of hydrogen is that it is easily catalyzed under mild conditions; at the anode, hydrogen is oxidized to liberate two electrons and two protons as shown in equation 2.1 below (Yuan et al, 2005):



The protons are conducted from the catalyst layer through the proton exchange membrane and the electrons travel through the electronic circuits. At the cathode, oxygen is reduced as presented in equation 2.2:



Combining equations 2.1 and 2.2 gives equation 2.3, which is the overall cell reaction:



Reactions shown in equations 2.1 and 2.2 can be catalyzed by platinum or ruthenium on carbon black support, to minimize the carbon monoxide poisoning at the cathode, while the carbon black support increases the surface area of the heterogeneous catalyst area to increase utilization.

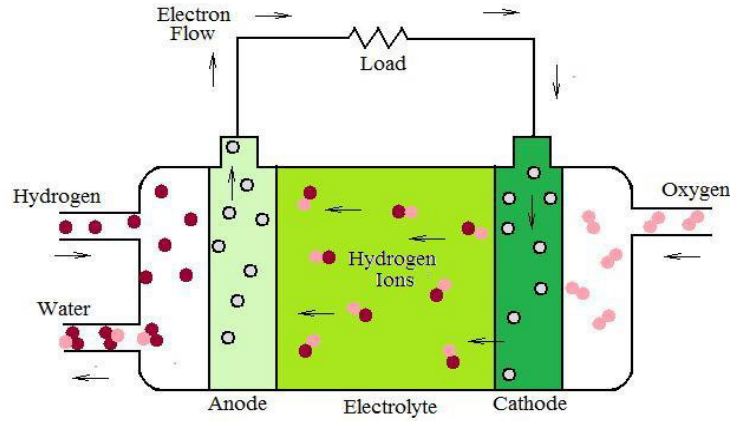


Figure 2.6: Proton Exchange Membrane Fuel Cell (PEMFC)

The relative ease of the oxidation of methanol at the anode to liberate protons and electrons makes it an attractive source of fuel (Jeng and Chen, 2002). Compared to hydrogen fuel cells, DMFC is further advantageous for its ease of fuel delivery, storage, and lack of humidification requirements, as well as its reduced design complexity and high power density (Kulikovsky, 2003; Sandhu et al, 2005; Schultz and Sundmacher, 2005; Schlake et al, 2006; Chen et al, 2006). Despite these compelling advantages, DMFCs are nevertheless hampered by the low electro-activity of the methanol oxidation at the anode, and the large amount of undesired methanol transported through the PEM from the anode to the cathode. This is referred to as methanol crossover, and it continues to be problematic (Ge and Liu, 2005; Kjeang et al, 2006; Thomassin et al, 2006; Oedegaard and Hentschel, 2006). In direct methanol fuel cells, the solution of methanol and water is fed to the anode where it is internally reformed by the catalyst and oxidized to liberate electrons and protons as follows (Shukla et al, 2002; Xu et al, 2005; Sandhu et al, 2005):



The cathode reaction for DMFC is similar to a hydrogen fuel cell:



Combining equations 2.4 and 2.5, gives an overall cell reaction:

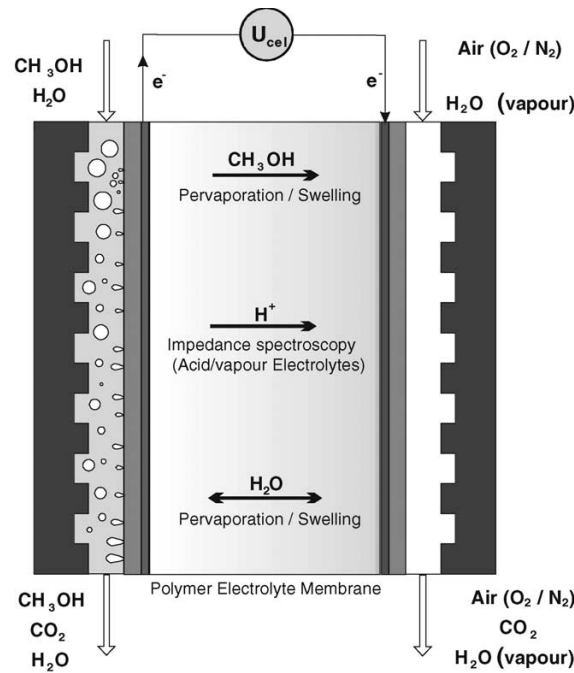


Figure 2.7: Direct Methanol Fuel cell (DEMFC) (Silva et al., 2005)

2.2 Thermodynamics of Proton Exchange membrane Fuel Cell

Thermodynamics of PEMFC provides information on the amount of energy produced by fuel cell. Gibbs free energy, which is the energy available to do external work regardless of changes in pressure and volume, plays an important role in the thermodynamics of

energy conversion in proton exchange membrane fuel cell (Matelli and Bazzo, 2005). The conversion of energy into electricity in most electrical devices is simple and straight forward; however it is much more difficult in the case of the fuel cell (Dohle et al, 2002), considering the nature of energy outputs and inputs as shown in Figure 2.10. The movement of the electron around the external circuit of the fuel cell determines the external work done on the fuel cell; any work done as a result of the change in volume between inputs and outputs energy does not affect the amount of external work done as this change is not harnessed by the fuel cell (Matelli and Bazzo, 2005). All forms of energy shown in Figure 2.8 are chemical, although they behave rather like mechanical potential energy in two ways. Firstly, in an energy conversion system that results from a chemical reaction, there is a point where the energy is zero: namely the pure elements can be defined as being in normal state at standard temperature and pressure.

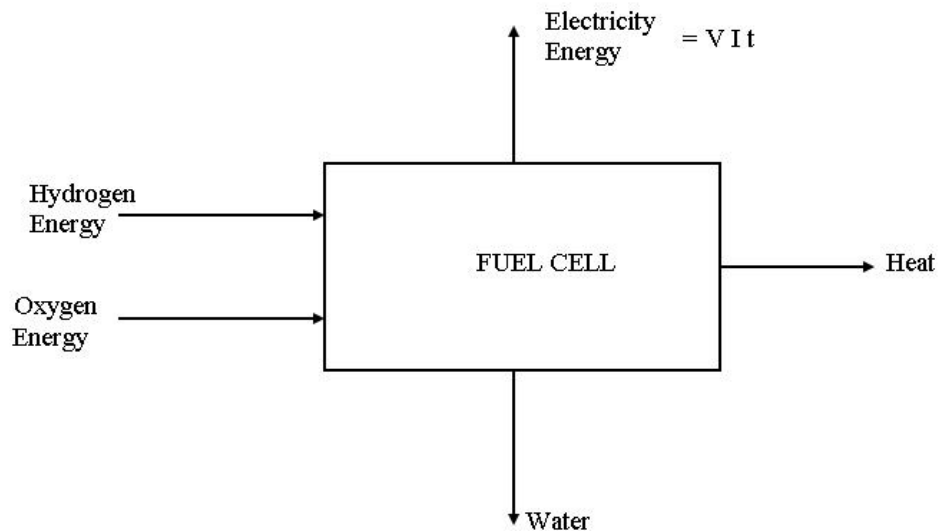


Figure 2.8: Energy inputs and outputs (energy balance) in fuel cell (Iyuke et al, 2003)

At this point Gibbs free energy of formation (G_f) is used to describe the external work done instead of Gibbs free energy reaction (G). Also enthalpy of formation is used rather

than enthalpy of reaction. Therefore, in a proton exchange membrane fuel cell it is the change in the Gibbs free energy of formation ΔG_f that produces the energy released, and this change is defined as the difference between the Gibbs free energy of formation the products and the Gibbs free energy of formation of the inputs of electrochemical redox reactants used in generating the energy. This is shown in the reactions listed below:



From the reaction above, the Gibbs free energy of formation ΔG_f can be evaluated using Equation 2.9 (Matelli and Bazzo, 2005):

$$\Delta G_f = \Delta G_f \text{ of products} - G_f \text{ of reactants} \quad (2.9)$$

Equation 2.9 can be expressed in terms of mole as:

$$\Delta g_f = g_f \text{ of products} - g_f \text{ of reactants} \quad (2.10)$$

$$\Rightarrow \Delta \bar{g}_f = (\Delta \bar{g}_f)_{H_2O} - (\Delta \bar{g}_f)_{H_2} - \frac{1}{2}(\Delta \bar{g}_f)_{O_2} \quad (2.11)$$

The Gibbs free energy of formation does depend on the temperature and state of the reactants. Secondly, a consideration of the chemical energy conversion in fuel cell as a mechanical potential energy makes it possible to assume that the process in a fuel cell is irreversible; i.e. There are no heat losses in the fuel during the course of the conversion of chemical energy to electricity. If this is the assumption, then all the Gibbs free energy is converted into electrical energy, even though in real life practice, some of this energy is released as heat. This assumption implies that the electrical work done in moving the

charge from the electrochemical reaction round the circuit is equal to the Gibbs free energy released in the course of the reaction. Therefore (Qi et al, 2005),

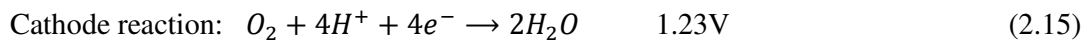
$$-\Delta \bar{g}_f = -2FE \quad (2.12)$$

Where: F = Faraday constant (charge on one mole of electrons), E = Voltage of the fuel cell.

From equation 2.12:

$$E = \frac{-\Delta \bar{g}_f}{2F} \quad (2.13)$$

Equation 2.13 evaluates the electro motive force (emf) of the reversible open circuit voltage of the H₂ fuel cell, based on the assumption stated above. But if the cell were perfect in transferring the energy resulting from the formation of water as shown in equations 2.14-2.16, it would create 1.23V with little heat generated (Larminie and Dicks, 2001):



It can be observed from equations 2.14-2.16 above that the open circuit potential of a fuel cell operating under ideal conditions is 1.23V at 25°C, which is the representation of the result, generated from equation 2.14, and is known as theoretical voltage (Larminie and Dicks, 2001). Theoretically, voltage produced in a fuel cell depends on the operating temperature, number of electrons transferred and the free energy of the fuel used in fuel

cell (Kulikovsky, 2002). But there are some factors affecting the efficiency of the fuel cell that reduce the actual voltage. These factors are ohmic polarization, concentration polarization and activation polarization (Scott et al, 1999; Kulikovsky, 2002; Pei et al, 2006; Inoue et al, 2006), as shown in Figure 2.9. From the curve shown in Figure 2.9, it can be deduced that the theoretical open circuit potential represented by a dotted line is greater than the real open circuit potential represented by a solid line and that it also decreases with an increase in current density. The efficiency of the fuel cell can thus be improved so as to generate more voltage if the above factors can be improved. However, the thermal stability of the membrane militates against operating the fuel cell at a high temperature.

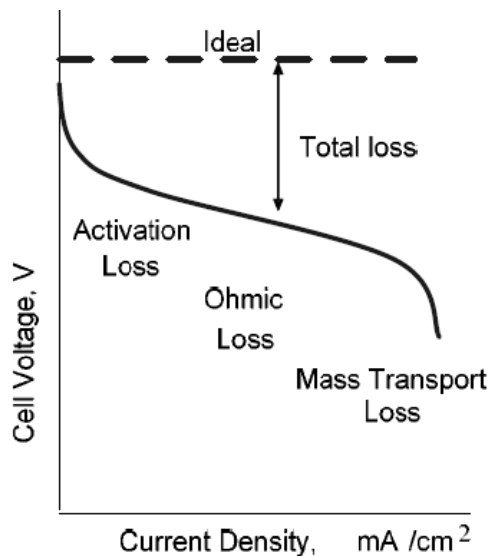


Figure 2.9: I-V Characteristic of fuel cell showing various losses (Larmine and Dicks, 2001)

Activation polarization is a product of energy activity in the fuel cell, involving the making and breaking of chemical bonds at the cathode and anode as shown in equations 2.14-2.16. The resulting ions from the electrochemical redox reaction at the anode bonds

with the catalyst surface, while the electrons remain near the ions until another molecule from the fuel reacts with a catalyst, resulting in the bond breaking with the ion (Sousa Jr and Gonzalez, 2005; Roshandel et al, 2005). The energy input for the bond breaking determines whether the electron will bond against the ion or remain separate. Also, at the cathode, the incoming oxygen is broken up as shown in Equation 2.15 and draw electrons, ions and oxygen atoms to form water. The quantity of energy required for the breaking and making of these bonds at the anode and cathode comes from fuel, and results in the reduction of overall energy produced by the cell. This overall energy reduction can be controlled by increasing the reaction rate in the cell, which leads to an increase in the kinetic energy of the reactants, thus lowering the energy required to break the bonds. Apart from the activation energy barrier at the electrode that results in activation over potential, water produced in the cell also contributes to the activation polarization. The water produced covers the surface of the electrode and thus limits the access of gas to the catalyst layer. Hence, the increasing temperature, maximizing of the electrochemical active surface area and utilization of fuel will lower the effect of activation polarization. A further contributing cause of the potential loss arises from electrical losses in the cell (Roshandel et al, 2005; Ogaji et al, 2006) and is the result of resistance over voltage, also known as ohmic polarization. The common form of ohmic polarization comes from the flow of electric current through an electrolyte, current collecting plate and electrodes. The contribution of the electrolyte to ohmic polarization arises from the resistance to ionic flow; the resistance from the electrode is the result of the contact resistance between the current collector, and the electrolyte and electrode material itself. Different methods of energy retrieval from the cell also contribute to ohmic polarization. The total resistance arising from ohmic polarization is therefore given as (Argyropoulos et al, 2003; Roshandel et al, 2005; Kulikovsky et al, 2005):

$$R_T = R_M + R_{ec} + R_i \quad (2.17)$$

Where: R_M = ionic resistance of membrane, R_{ec} = electronic contact and material resistance of electrode and graphite block, R_i = ionic contact resistance between the membrane, electrode and the electronic resistance of the electrode

Therefore, a membrane with a lower resistance can be employed to improve R_T in the fuel cell and this can be achieved via a thinner membrane. Another way of improving R_T is by optimizing the electrode preparation and operating conditions of the fuel cell.

Another form of voltage loss in fuel cells is termed concentration polarization, and is a result of the poor mass transport of the reactant at a high current density (Kulikovsky, 2002). Though its contribution to total energy loss in the fuel cell is small, it cannot be neglected, mainly because it arises from concentration changes induced on the electrode by electro chemical reactions (Kulikovsky et al, 2004). Concentration polarization can be reduced by using a high surface area electrode and thinner electrodes that can shorten the path of the gas to the sites. Increasing the gas pressure, which drives the water in the cell and fuel concentration, will also reduce the concentration polarization (Haraldsson and Alvfors, 2005; Hernandez-Pacheco et al, 2005).

2.3 Proton Exchange Membrane

Proton exchange membrane is defined as an inter-phase between two adjacent phases, i.e. fuel and electron, which acts as a selective barrier by regulating the transport of substance between the two compartments (Ulbricht, 2006). Ion exchange membranes are classified into anion and cation exchange membrane, which is further divided into strong acid, weak acid, strong base and weak base, depending on the type of ionic group attached to the membrane matrix (Larminie and Dicks, 2001; Chen et al, 2004;

Xu, 2005). Cation exchange membranes contain negatively charged groups i.e. $-SO_3^-$, COO^- etc; these allow the passage of cations while anions are rejected. The anions exchange membrane, on the other hand, contains a positively charged group such as NH^+ , NRH_2^+ , PR_3^+ etc (Xu, 2005) attached to the membrane backbone and allows the passage of anions and the rejection of cations. Out of the four types of membrane, strong acidic and strong base types are most highly ionized and possess higher ionic conductivities resulting from the migration of H^+ and OH^- ions (Ulbricht, 2006). Consequently, these types of membranes are of great interest in fuel cell applications. Generally, an ion exchange membrane saturated with unbound electrolyte solution gives some of the quality of PEMFC. Also affecting the physical properties of the membrane is the unit which forms the polymer backbones in ion exchange membrane. It is divided into two. The first one is the condensation polymer, which is the product of the reaction between formaldehyde and phenol that contains the ionizing constituents on the para-position of each aromatic ring (Ulbricht, 2006). The second type is the one produced from co-polymer and normally consists of a third region, which influences the qualities of the membrane.

Historically, in 1850 Way and Thompson reported their work on the discovery of ion exchange membrane as a property of some clay minerals. This was after the first fuel cell was invented by Grove in 1839 (Larminie and Dicks, 2001). The use of ion exchange membrane as an electrolyte in a fuel cell was originally described by Grybb in 1952 (Ulbricht, 2006; Li, 2006) and, since then, research and development in the area of membrane for fuel cell applications has lead to the production of Nafion[®] by Dupont in 1968 and some other commercial membranes (Smitha et al., 2005). Before the advent of these membranes, the polymer electrolyte consisted of sulphonated poly

(styrene divinylbenzene) co-polymers. But oxidative degradation of the polymer backbone resulted in a poor life time of this membrane. The success of the Dupont and Dow Chemical Company in synthesizing perfluorinated sulphonic acid membrane has contributed immensely in the development of polymer electrolyte membrane for fuel cell applications. Generally, Nafion[®] consists of fluorocarbon polymer backbone as shown in Figure 1.1, with chemically bounded acid groups. The attached acid molecules are fixed to the polymer; because of this it cannot be leached out, but can allow the free migration of the proton through the electrolyte. Therefore, Nafion[®] exhibits an acid strength equal to that of 1M sulphuric acid. Typically, Nafion[®] is about 50-200µm in thickness and can be handled safely and easily (Wilson and Gottesfeld, 1992; Mehta and Cooper, 2002). The comparison of Nafion[®] with other commercially available membranes, i.e. Aeplex-S[®] and the Dow, show that the latter give better performance (Smitha et al, 2003). This is attributed to low resistance and a large number of sulphonic acid groups attached to the main chain, resulting in higher conductivity. The thinner nature of Nafion[®] gives it a better performance in fuel cell applications. Therefore, high chemical stability, low density, high mechanical strength and high conductivity are Nafion[®]'s greatest strengths, securing high durability in fuel cells (Xing et al, 2004). High cost, availability, low thermal stability and high sensitivity to Carbon (ii) oxide are its major disadvantages (Smitha et al, 2003; Kim et al, 2003; Xing et al, 2004; Chen et al, 2004).

Despite all the problems associated with the Nafion[®], it is still the most popular commercially available membrane for fuel cell applications. However, there are other commercial membranes, such as, for instance, the membranes produced by Ballard Power System and W.L Gore & Associate. Ballard's development of the membrane power system began in 1998 and their objective was to identify less expensive polymers

exhibiting similar properties to Nafion[®]. In achieving this objective, the organization focused on the post sulphonation of thermally stable polymers such as polystyrene, poly (trifluoro styrene), etc. Ballard achieved their goals but durability of the products remains a problem and affects the availability of their membrane. Consequently, Ballard does not sell their membrane on the commercial market, although it is available for the in-house manufacturing of fuel cell stacks. Contrary to Ballard Power System, Gore membranes are available commercially (although they do not make fuel cells or stacks) and are utilized by some fuel cell companies. Gore & Associates' membranes were introduced in 1995, and their product is GORE-TEX impregnated with Nafion. The compatibility of the two polymers is the result of the fact that GORE-TEX and Nafion[®] are fluorinate polymers. High ionic resistance, resulting in low proton conductivity and differential swelling between GORE-TEX and Nafion[®], is its major disadvantage. On the other hand, rigidity, hydrophobic and porosity, all desirable properties of membrane in fuel cell applications, give the Gore membrane greater strength and less swelling than Nafion[®] membranes. The Dow chemical membrane, manufactured by the Dow Chemical Company (DOW), is similar to Nafion[®]. All the above represent efforts to produce high quality membrane that can compete with Nafion[®] and other commercial membranes, and researchers and other agencies continue to be interested in exploring synthesised membranes from different sources and methods. Hence with the available literature (Tsui et al, 2007; Kato et al, 2007; Sahu et al, 2008) on membrane preparation and development, it was observed that little has been achieved in synthesising membrane from the locally available polystyrene butadiene rubber with no information on blending the membrane with carbon nanoballs.

2.4 The Membrane Electrode Assembly

The catalyst and the membrane are parts of the basic unit of fuel cells which are bonded together into one component and referred to as the Membrane Electrode Assembly (MEA) (Park et al., 2008). The MEA is the heart of the fuel cell (Iyuke et al, 2003; Park et al, 2008), and consists of a sheet of proton – conducting polymer electrolyte membrane with two electrically and ionically conductive electrodes containing the platinum catalyst bonded to the opposite sides of the polymer sheet as shown in Figure 2.10 . Typically, there are two popular ways of bonding the electrodes to the proton exchange membrane. Firstly, the catalyst can be sprayed directly onto the membrane and dried to form the electrode on its surface (Cho et al, 2008). Secondly, the prepared catalyst can be sprayed on carbon black and hot pressed on both sides of the membrane (Hickner, 2003; Rajalakshmi and Dhathathreyan, 2007; Park et al, 2008; Cho et al, 2008). The arrangement, i.e. the bonded membrane electrode, is then compressed on both sides by the grooved bipolar plates or grooved end plates in the case of the single cell so as to transport the H_2 and O_2 /air respectively to the electrode (Therdthianwong, 2007; Wiles et al, 2007).

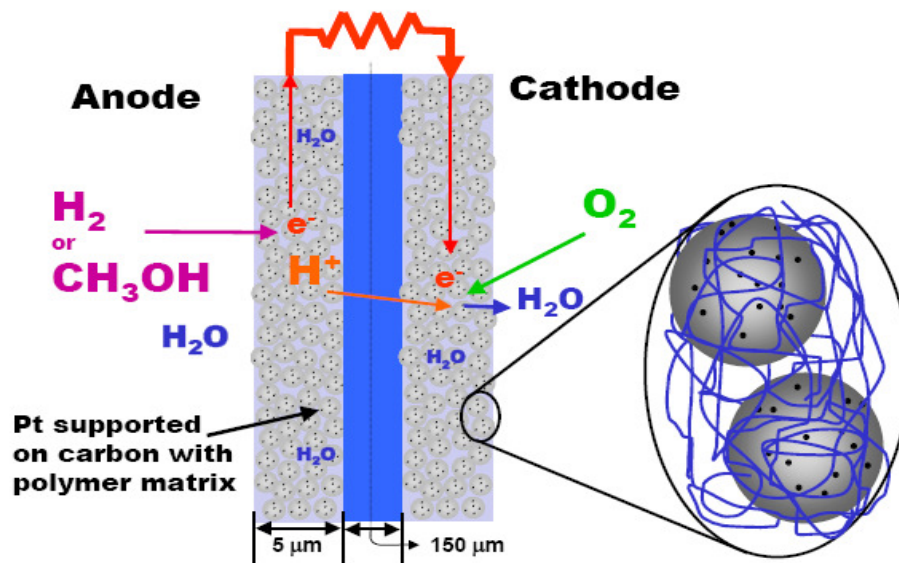


Figure 2.10: Schematic of Membrane Electrode Assembly (MEA) (Hickner, 2003)

The proton exchange membrane, also referred to as the electrolyte, serves as an ion conductor between electrodes. The electric insulator nature of the polymer membrane back bone and acid groups attached to the membrane are responsible for the ability of the membrane to prevent electrons from moving from anode to cathode. Electrons produced as a result of electrochemical reactions shown in Equations 1.1 – 1.3, only travel from a reaction site in the anode through the diffusion layer to the reaction site in the cathode. This is due to the presence of loosely held electrons at the reaction of the electrodes. The mechanism of movement of electrons through the diffusion layer involves the collision of electrons with the molecule of diffusion layer material, which releases their energy to the molecule, resulting in the exciting of the diffusion layer of the material molecules. The excited molecule then releases an electron which collides with another molecule. The membrane does not allow electrons to flow through, but the ions produced at the anode are transported across the membrane to the reaction sites in the cathode. The

transport process of the ions involves their interactions with each other as well as with the water molecules (which is the by-product of the electrochemical reaction in the fuel cell) in the membrane. The acid chain in the membrane does not contribute directly to the ion transport process, but maintains the structural integrity and electronic insulator of the membrane. The positive potential as a result of buildup of hydrogen at the anode – membrane interface is the initial force that is required to move the ions. While the membrane serves the purpose as stated above, electrodes perform three functions, as listed below (Wilson and Gottesfeld, 1992; Haynes, 2001; Mehta and Cooper, 2002):

1. The electrodes act as a physical barrier between the gaseous stream and the solid electrolyte.
2. The electrodes supply a surface site where ionization and de – ionization of fuel and oxidant may occur.
3. The electrodes provide a porous interface between ions in the gaseous streams and the ion conducting electrolyte.

The electrodes can contain either an unsupported (methanol fuel cells) or supported (hydrogen fuel cells) catalyst and are usually composed of the same copolymer as the proton exchange membrane (Hickner, 2003; Biyikoglu, 2005). Depending on the area of application, the amount of catalyst per active area and the ionomer content of the electrode which is referred to as catalyst loading can vary between 5-20 weight percent. Generally, there are two electrochemical reactions that occur in the MEA as explained earlier in section 1.1: an oxidation half-reaction at the anode and a reduction half-reaction at the cathode (Marr and Li, 1998; Wang et al, 2000; Towne et al, 2007). Normally, the two half-reactions would occur very slowly at the low operating temperature of the PEM fuel cell. Each of the electrodes is coated on one side with a

catalyst layer that speeds up the reaction of oxygen and hydrogen and is usually made of platinum powder very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen (Towne et al, 2007). The platinum-coated side of the carbon paper faces the proton exchange membrane. Platinum-group metals are critical to catalyzing reactions in the fuel cell, but they are very expensive (Daiko et al, 2006). There is a wide spread global effort to reduce the use of platinum in fuel cell cathodes by at least a factor of 20, or to eliminate it altogether to decrease the cost of fuel cells to consumers. The numerical evaluation of the quantity of hydrogen required by the process to occur in the fuel cells operation can be simulated by using the half reaction at the anode. Also, the combination of half reaction at both the cathode and anode can be used to numerically determine the amount of oxygen required and water produced by the process (Wang et al, 2000).

The efficiency of the MEA is greatly influenced by the thickness, which depends on the thickness of the membrane and catalyst. The membrane thickness in a MEA can vary depending on the type of membrane, while the thickness of the catalyst layers is a function of the platinum (Pt) loading on each electrode. Also affecting the efficiency of MEA is the backing layers (also known as diffusion layers), flow field and current collector. The purpose of the backing layers, flow fields, and current collectors is to maximize the current from a membrane/electrode assembly. The diffusion layers are placed next to the electrode and are usually made of a porous carbon paper or carbon cloth, about as thick as 4 to 12 sheets of paper. The ability of carbon materials to conduct electrons that leave anode to cathode favours their choice as backing layer. The porous nature of the diffusion layers ensures the effective diffusion (flow of gas molecules from a region of high concentration to a region of low concentration) of each reactant gas to the catalyst on the membrane/electrode assembly. It also allows the gas to spread out as

it diffuses through the layers for effective contact with the entire surface area of the catalyzed membrane.

The diffusion layers also help in managing water in the fuel cell. Water is essential in a fuel cell and low or higher volume water can cause the cell to stop operating (Roshandel et al, 2005; Kim et al, 2006). Water can build up in the flow channels of the plates or can clog the pores in the carbon cloth (or carbon paper), thus preventing reactive gases from reaching the electrodes. Diffusion layers control the amount of water vapor to reach the MEA and keep the membrane humidified. Water transport is a very important property of the ion exchange membrane in fuel cell applications, relating to the electro-osmotic transport of water by the conduction ions and back diffusion of water immediately the gradient is established. The tendency of the migrating ions to carry water to one side of the membrane, resulting in a higher resistivity region in the water poor side, makes water migration in the ion exchange membrane important. In addition, the diffusion functions as a water regulator in the fuel cell. In order to prevent the pores in the carbon cloth from becoming clogged with water, thus hindering the rapid gas diffusion necessary for a good reaction rate at the electrodes, the diffusion layers are often coated with TeflonTM (PTFE). This does not influence the thickness of the MEA. This polymer (Teflon) is a fluorine substitute of polyethylene $(-\text{CF}_2-\text{CF}_2-)_n$ and it serves as an insulator and binder in fuel cells (Sopian and Wan Daud, 2006). It is white, solid with a waxy appearance, possesses good resistance to heat and can survive temperatures in the range of 160-280°C; it decomposes around 370°C to liberate an explosive monomer. Therefore, the incorporation of TeflonTM by mixing it into the diffusion or catalyst layer serves two functions; binding the high surface carbon particles into a cohesive layer and also imparting a slightly hydrophobic character to the layer. It also helps in preventing liquid water from blocking the pores of the diffusion layer (Wang et al, 2005).

A piece of hardware known as a bipolar plate that serves as a flow field and current collector is pressed against the outer surface of each diffusion layer (Sopian and Wan Daud, 2006). The plates are made of a lightweight, strong, gas-impermeable, electron-conducting material: graphite or metals are commonly used, although composite plates are now being developed. In a single fuel cell, these two plates are the last of the components making up the cell. The first task served by each plate is to provide a gas flow field (channels), which is etched into the side of the plate next to the diffusion layer (Wan and Wang, 2006). The channels carry the reactant gas from the place where it enters the fuel cell to the place where it exits. The pattern of the flow field in the plate (as well as the width and depth of the channels) has a large impact on how evenly the reactant gases are spread across the active area of the MEA. The design of flow field also affects the water supply to the membrane and water removal from the cathode; hence the need to carefully design the bipolar plate to be used in fuel cells application.

2.4.1 Fabrication of membrane electrode assembly

The electrodes (anode and cathode), catalyst, and polymer electrolyte membrane together form the membrane electrode assembly (MEA) of a polymer exchange membrane fuel cell. The anode, which is the negative side of the fuel cell, conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit. Channels etched into the anode disperse the hydrogen gas equally over the surface of the catalyst. The cathode, that is the positive side of the fuel cell, also contains channels that distribute the oxygen to the surface of the catalyst. It conducts the electrons back from the external circuit to the catalyst, where they can recombine with the hydrogen ions and oxygen to form water. The polymer electrolyte membrane (PEM)—a specially treated material that looks like ordinary kitchen plastic wrap—conducts only positively charged

ions and blocks the electrons. The PEM is the key to fuel cell technology: it must permit only the necessary ions to pass between the anode and cathode. Other substances passing through the electrolyte would disrupt the chemical reaction. Researchers have employed different methods for the preparation of the MEA, each exhibiting different merits and demerits depending on the nature of the polymer. For instance, Chen et al (2008) developed a novel MEA for utilized regeneration fuel cell. It was prepared by a Nafion-pyrolysed method of MEA preparation, according to which the electro catalyst was sprayed directly onto each side of the Nafion and dried for 24 hours at room temperature. The results of Chen et al's findings revealed that the prepared MEA showed a high water electrolysis performance and a much higher fuel cell performance than that of the conventional MEA.

Also in 2008, Oslon and co-workers reported their work on the preparation of the MEA using a non-platinum cathode catalyst. The objective of their research was to reduce the cost of proton exchange membrane fuel cell by reducing the cost of the catalytic layers of the MEA. They achieved this by employing alternative ultra-low precious metal loading that met the performance specification of expensive platinum. The group evaluated the performance of different layers of the nano-structured template of non-platinum electro catalysts for proton exchange membrane fuel cell. Their findings also revealed that the performance of non-platinum was better than that of platinum catalyst and that the loading of 4 mg/cm^2 was optimal. Similarly, Bayrakceken et al (2008) presented their work on the effects of the MEA components on PEM fuel cell performance. Factors investigated by the group were membrane thickness, the hot pressing conditions of the gas diffusion layer and Teflon and the carbon ratio on the gas diffusion layer. The results of their findings revealed that fuel cell performance was inversely proportional to the membrane thickness. The Teflon and carbon ratio in the gas diffusion layer were directly

proportional to the fuel cell performance up to a certain value. Further increase of the Teflon and carbon ratio in the gas diffusion layer reduced the cell performance. The group also reported that the optimum hot-pressing conditions of the catalyst coated gas diffusion layer onto the membrane were 172N/cm^2 . Their results also showed that the hot pressing of the gas diffusion layer onto the 3-layer MEA decreased the fuel cell performance. The best performance was achieved when the gas diffusion layers were pressed directly on the MEA. Krewer et al (2008) presented a model that predicts the effect of diffusion layer and membrane properties on the electrochemical performance of direct methanol fuel cell MEA. They achieved their aim by varying the properties of single layers of the MEA. The results of their analysis conducted on the fabricated MEA enabled them to identify the influence of the layer's properties on the electrochemical performance and methanol crossover. It was also reported that the membrane with lower diffusivity combined with a thicker anode micro-porous layer leads to MEAs with lower methanol crossover. In 2005, Wang et al developed and evaluated humidifying MEA with water transfer region. When compared with conventional MEA, the MEA developed by the group showed a significant improvement in cell performance. Their self humidifying MEA also produced power density of 85 mW/cm^2 at 0.5 V. This value was two times higher than that of a conventional MEA. The factors that influenced the performance of their MEA were hydrogen flow rates, environmental temperature and humidity. The results of their findings showed that the best cell performance was obtained at 40 ml/min hydrogen flow rate, while the high environmental temperature yielded relatively good cell performance. The cell voltage was slightly decreased as the environmental humidity increased. The results also indicated that the developed MEA with a water transfer region area of about 28 % was the best for practical application. Therdthianwong et al (2007) investigated the effects of hot-pressing parameters on the

MEA. The group employed a 2ⁿ factorial design to investigate the effect of time, temperature and pressure on the performance of MEA. The results of their investigations showed that temperature was the most important parameter, followed by pressure, time-temperature, and pressure-time-temperature interaction. The MEA prepared at a hot pressing condition of 1000 psi, 100°C and pressing time of 2 minutes resulted in better fuel cell performance. Wan et al (2007) reported the performance of an MEA developed from metal – based integrated composites for application in direct methanol fuel cell. The group aimed at integrating the multi-functions of a conventional MEA, gas diffusion layer and current collector to fabricate an improved MEA. This was achieved by impregnating the Nafion electrolyte onto a sandwiched structure containing expanding-poly tetra fluoro ethylene and porous titanium sheets. The resultant composite electrolyte was coated with a catalyst and micro porous layer. The fabricated MEA was then tested in a direct methanol fuel cell stack. Performance results indicated that an ethanol feed of 2 moles at ambient pressure yielded a maximum power density of 19 mW/cm² at 26°C. Jung et al (2007) reported their work on the influence of annealing on the performance direct methanol fuel cell. The results of their research indicated that annealing at 130°C was closer to the glass transition of the recasted Nafion binder and provided higher proton conductivity. The MEA prepared at an annealing temperature of 130°C resulted in the best electrochemical active surface area. The groups have thus arrived at a useful tool for enhancing the MEA performance in fuel cell. Kim et al (2006) proposed a novel structure of MEA to achieve high performance in a passive direct methanol fuel cell. The group developed a nano-composite MEA with low methanol crossover. The results of their investigation into the effect of the water back diffusion layer on the performance of the MEA indicated that this novel composite provided a power density of 48mW/cm² at 0.3 V, which was 1.5 times higher than that of a conventional MEA. They attributed the

higher power density exhibited by the MEA to low methanol crossover. This modified MEA proved suitable for application in the mobile energy source.

Similarly, Luo et al (2006) investigated the degradation of MEA in a single cell with an active area of 4 cm^2 . The MEA developed by the group was tested in a stack for 200 hours at ambient humidity, ambient pressure and 60°C . The results of their findings revealed that the platinum catalyst MEA decays faster than the carbon supports. They attributed this to the possibility of platinum missed metal particles when the contact carbon layer has been corroded. The decay of the catalyst was more serious than that of the membrane. The membrane lost its proton conductivity ability and the iron element dissociated from the perfluoro carbon chains. Pan et al (2005) fabricated an unusual structure MEA by the electrostatic self assembly between the positive charged platinum-poly (diallyl dimethyl ammonium chloride) nanoparticles and the sulphonic acid group at the Nafion membrane interface. The novel MEA generated 2.3 mW/cm^2 power densities at room temperature and platinum loading of $2.8 \mu\text{g/cm}^2$. The results of their findings also indicated that the charged Pt-PDD nanoparticles formed a monolayer on the Nafion surface. Such formation of a monolayer might be very useful in the development of a proton exchange membrane fuel cell with controlled surface. Park et al (2008) investigated both the physical and electrochemical properties of MEA fabricated using a hydro-carbon based polymer as electrolyte by varying the content of ionomer binder in the catalyst electrode. The results of their findings indicated that the property of fabricated MEA was similar to that of conventional MEA. Wan and Wang (2006) also proposed the concept of an integrated MEA. The fabricated MEA with a finely porous metal sheet and E-PTFE substrate was proven to have characteristics that compared well with conventional MEA. The fabricated MEA produced maximum and stable power density of 80 mW/cm^2 . The group concluded that the fabricated MEA exhibited a unique

characteristic that makes it a suitable candidate in a small fuel cell application and commercialization. Selvarani et al (2007) reported on a method devised to anchor phenyl-sulphonic acid functional groups with platinum catalyst supported on a high surface area carbon substrate. The MEA was made by hot pressing the cathode and anode onto either side of a pretreated Nafion-membrane at 25 kN and 130°C for 3 minutes. The performance of the fabricated MEA was investigated and the results indicated that the phenyl-sulphonic group anchored on the carbon support of the platinum catalyst improves the performance of the fuel cell. Their results also showed that the anchored phenyl-sulphonic acid groups modified the oxidation state of platinum which improved oxygen reduction kinetics. Gustavsson et al (2007) prepared MEA by depositing platinum and titanium oxide directly onto the Nafion membrane using a thermal evaporation method with varying deposition order and thickness. The results of their investigation into the MEA revealed that performance increased with the presence of a thin layer of titanium oxide when compared with that of a platinum film deposited directly onto the Nafion. Their findings also indicated that the film thickness and deposition order influence the MEA performance. Pozio et al (2002) developed a technology for making a membrane electrode gasket assembly (MEGA) for application in proton exchange fuel cells. They achieved this by sealing the MEA in a molded gasket of different shapes. The results of their investigation showed that MEGA technology possessed several advantages with respect to traditional proton exchange fuel cells. Some of the advantages of MEGA technology include: effective membrane saving, reduction in fabrication time, quality control and failed element substitution. Towne et al (2007) fabricated MEA using inkjet print technology. The group employed commercial desktop inkjet printers to deposit active catalysts from the printer cartridge onto Nafion membrane. They suggested that inkjet print technology could reduce the cost and time of

MEA fabrication. The results of their findings revealed that the fabricated MEA produced an open circuit of 0.87 V and power densities of up to 155mW/cm^2 with a catalyst loading of $0.20\mu\text{g/cm}^2$. It can be seen that the coupling of membrane and electrode to form a unit was the final step in the fabrication of the membrane electrode assembly and researchers have adopted various methods in this regard. All the methods were therefore tailored towards fabricating a unit that would produce an efficient membrane electrode assembly. Hot pressing methods will therefore be employed in this research for MEA fabrication using the membrane synthesized from polystyrene butadiene rubber and a platinum catalyst deposited on carbon nanotubes support

2.5 Tape Casting

Tape casting, also known as doctor blading, is described as a forming technique employed for producing thin and flat ceramics in the range of $25\text{ }\mu\text{m}$ to 1 mm thickness. In some cases a thickness of $5\text{ }\mu\text{m}$ is also possible depending on the starting slurry and setting of the doctor blade gauge. Tape casting technique was originally developed for the casting of electronic ceramic such as multilayer capacitors, insulating substrates and packages (Snijkers et al, 2004). It was reported that the technology of tape casting has long been employed in painting industries to test the covering power of the paint formulation (Petkov, 2007). Other applications of tape casting include the casting of membranes and components of solid oxide fuel cells. In present day ceramics technology, tape casting has become a popular and economic way of producing flexible green sheets in a wide range of thickness (Snijkers et al, 2007; and Akbulut and Sonmez, 2007). The green sheets produced can be fired as single sheets or they can be laminated into complex structures that can incorporate different ceramics or conductive metal layers. Although the fired tape casts are typically flat pieces, other shapes such as tube

can be made from tape casting. Tape casting operation involves the dispersion of ceramic powder in a liquid that typically contains polymeric binders. Therefore, the basic advantage of tape-casting derives from its ability to create large, thin and flat ceramic or metallic parts that are difficult to press and impossible to extrude (Mistler, 1998). Figure 2.11 illustrates a typical laboratory scale tape-casting machine designed to cast slurries in small scale production into homogenous tape. To determine the carrier tape force, the carrier film is unwound from a roll with an adjustable torque and the carrier tape is guided by the casting head where the slurry is deposited by doctor blade technique. The casting gauge can be adjusted easily with the aid of micrometer screws gauge, while the slurry is caused by gravity from the slurry vessel. For efficient drying, the machine is equipped with a hot air inlet or bottom plate heater.

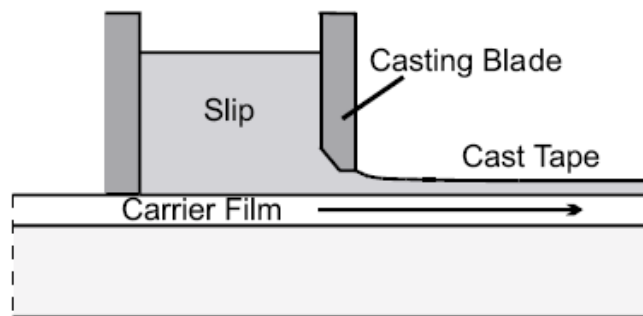


Figure 2.11: Tape casting machine

In the ceramic industries, slip casting is analogous to tape-casting because it is also a fabrication technique that uses the fluid suspension of ceramic as the starting point for processing; the difference is that tape-casting usually employs non-aqueous solvent as the liquid medium. The use of non-aqueous solvent in tape-casting techniques is the result of the drying process which is evaporative from the surface rather than absorptive into the plaster used in the slip casting. Also, lower cost, easy process control and the

possibility of reducing health and environmental hazards favour the choice of the tape-casting method, and especially water-tape-casting techniques (Meijester et al, 2004). While the drying rate is slow, the possibility of the components reacting or dissolving in water, and sensitivity to high cracks are factors that militate against the choice of water-tape casting techniques. To overcome such problems, polymer binders such as acrylic latex, celluloses and poly vinyl alcohol have been identified for tape casting, and their performance is influenced by their solubility in water (Petkov, 2007). The binders that are insoluble in water, such as acrylic latex, can be destroyed by a number of common stress processes, such as freezing or excessive heating during storage, and also mechanical stresses such as those encountered in the dispersion of ceramic powder. The resultant effect of these stresses is the formation of coagulate polymer that is not reversible, and which makes it difficult to re-dissolve and recast the large lump produced due to these stresses. Care must therefore be taken if acrylic binders are to be used in tape-casting. On the other hand, water soluble binders such as polyvinyl alcohol, which is dissolved in water with the dispersed ceramic, are typically stable to both mechanical and thermal stresses (Petkov, 2007). However, high slip viscosity is a major factor militating against their choice as the binders in tape-casting, and lower ceramic loading is therefore required in the liquid phase. The possibility of the hydroxyl groups in the binders reacting with ceramic additive is another disadvantage of water soluble binders, although the tape from the water soluble binders can be re-dissolved and re-cast, the implication is that the properties of the cast tape may be sensitive to humidity in the air which can lead to variation in the downstream processes. Other binder groups, such as the mixture of high molecular acrylic polymer with active groups, are generally considered the better binder (Petkov, 2007). The resulting product is a high molecular weight polymer with copolymerized active groups. It has been reported that the solubility

of the active group in the polymer is influenced by the addition of a small amount of base, such as ammonium hydroxide, which enables the dissolution of the binder active group in water before it can be used to cast tape (Petkov, 2007). The small amount of sodium hydroxide used to activate the binder evaporates with water during drying to produce ceramic tape that is insoluble in water and relatively insensitive to humidity. The positive feature of this group of binders is their ability to re-dissolve for re-casting if a small amount of ammonium hydroxide and water is added to the tape. Blending of the binder with the active groups makes the binder a very strong ceramics dispersant. The resulting strong dispersant ability of the binder enables higher green tape densities than those that can be achieved from the other binders mentioned earlier. In addition to the strong dispersant property, the addition of active group to the binder allows the complete dispersion of the nanoparticles to their base particle; however, this is a process that is difficult to achieve with aqueous and non-aqueous binders. The blending of the binders with active groups also makes it possible to control the viscosity of the binder and slip, while the base used in activating the active groups in the binder affects the properties of the tape and binder. Thus the, incorporation of active groups to the binder will eliminate the problems associated with the aqueous binder techniques. In comparison to the solve-based processing, low viscosity, high polymeric contents and internal plasticization coupled with the possibility of lamination at room temperature are the advantages of solvent-based tape-casting techniques over the superior binder (Petkov, 2007). The various stages involved in tape casting processing are depicted in Figure 2.12 a-c

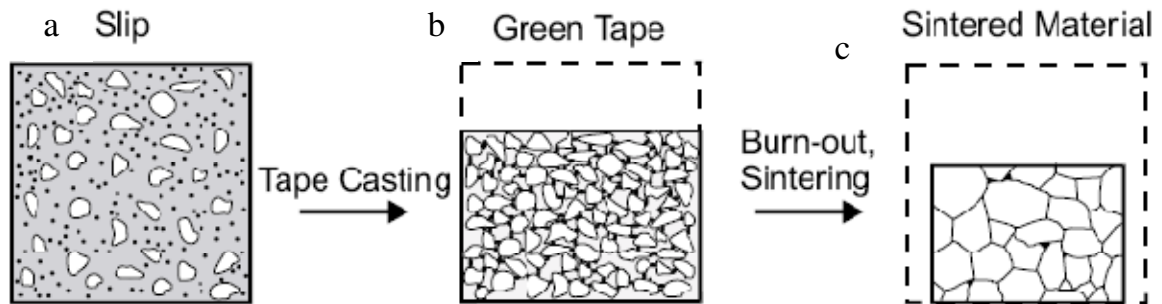


Figure 2.12: Stages involved in the processing of tape casting (Liversage, 2004)

Figure 2.12a represents the slip which consists of ceramic particles, water and binder in a proportion that depends on the desired quality and thickness of the products. Figure 4.2b represents the cast, a dried green sheet, which is characterised by its sensitivity to humidity and its excellent surface smoothness, flexibility and green density. Figure 4.2c shows the microstructure of the sintered material, which is the final product. The process flow tape casting technique employed in this research is shown in Figure 2.13:

The qualities of tape in tape casting technique are influenced by the doctor blade cast tape, which usually has a non-uniform density throughout the vertical axis due to particles and binder segregation. Non homogeneity of the tape is also a problem in the doctor tape technique and always leads to differential shrinkage and camber problems during sintering. The shrinkage variability is also a common problem in the production of tape by tape-casting technique and there are many variable factors that usually contribute to the shrinkage variability. These problems relate to raw material compositions, green tape density, sintering temperature and humidity.

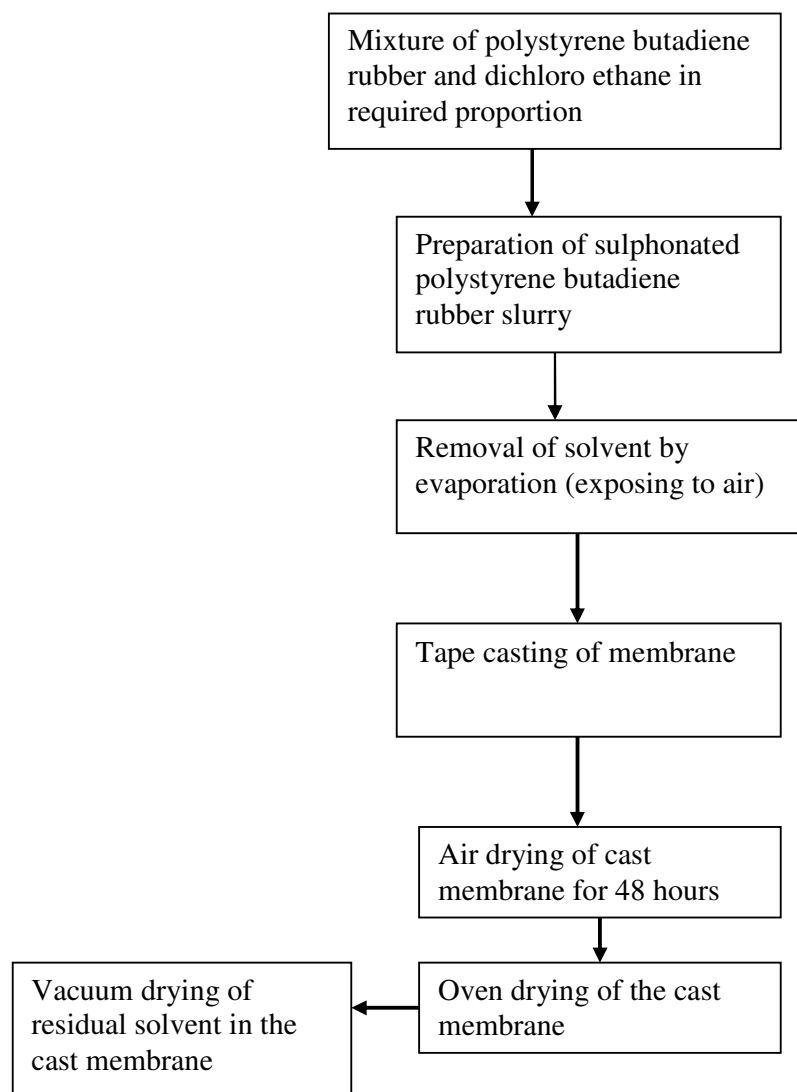


Figure 2.13: Process flow for tape casting of polystyrene butadiene rubber

The selection and proportioning of the slip components compositions are considered to be the major variables that affect the quality of the tape (Liversage, 2004; Perez and Carvalho, 2004). For instance, to prevent batch to batch variation in the preparation of the slip from resulting in the shrinkage variation of the tape, it is important to establish slip components that will ensure the highest quality of tape. In this work, the casting of membrane by the doctor blade technique begins with the investigation of the solubility of the sulphonated rubber in different solvents.

2.6 Carbon Nanoballs in the Development of Proton Exchange Membrane

Carbon nanoparticles i.e. carbon nanotubes, carbon nanoballs, carbon nanofibres, carbon nanohorns etc., are poised to make themselves the “materials of the millennium” due to their unique characteristics, such as good mechanical properties (Treacy et al, 1996; Liu, 2002), and good electrical conductivity (John et al, 1999; Kong et al, 2000; Saito et al, 2001; Ercok et al, 2006; Fan et al, 2007). The exceptional properties of these ‘miracle materials’, as they have been described by Karel (2006), have provoked the interest of many researchers, scientists and technologists from all parts of the world. Some of the applications of these materials pertain to energy storage (Che et al, 1999), hydrogen storage (Dillion et al, 1997; Liu et al, 2004; Haung et al, 2006), field emission (Yumura et al, 1999), nanoelectric devices (Fischer and Johnson, 1999; Hoenlein et al, 20003), artificial muscle (Hernadi et al, 1996), reinforcing materials (Kruger et al, 2002; Shaffer, 2004) and catalyst support in fuel cells (Rajesh et al, 2002; Matsumoto et al, 2004). These versatilities in carbon nanoparticle applications cause their price on the international market to be as high as five hundred US dollars per gramme (Iijima, 1991). Carbon nanoparticles, especially CNBs, have been receiving interest since their discovery in the 1940s (Kroto et al, 1985). Indeed, in the last two decades many different types of spherical carbons have been reported, both hollow and solid, and these include carbon onions (Ugarte, 1992), carbon microspheres (Kang and Wang, 1996; Kang and Wang, 1997; Sharon et al., 1998), carbon beads (Kamagawa and Yoshida, 1997; Inagaki et al, 1988; Wang et al, 1999) and carbon pearls (Birò et al, 2004). The type of spherical particle produced is dependent on the method of preparation, carbon source and the reaction conditions (Kang and Wang, 1996; Kang and Wang, 1997; Sharon et al, 1997; Kamagawa and Yoshida, 1997; Inagaki et al, 1988; Wang et al, 1999). These spherical materials have many potential applications, including use as absorbents (Vignal et al,

1999; Inagaki et al, 1999), as catalyst supports (Auer et al, 1998) and as anodes for use in lithium ion batteries (Sharon et al, 1997; Flandrioas and Simon, 1999).

Large scale production and high purity are important criteria for the industrial application of carbon nanoballs. Hence, high purity and non-conducting favoured the choice of CNBs in this work. Production techniques such as laser ablation and arc discharged are known to produce carbon nanoparticles, but on either a small scale or with a high content of impurity (Seo, et al, 2003) while catalytic chemical vapour deposition (CCVD) and the swirled floating catalytic chemical vapour deposition (SFCCVD) have been identified as the best methods to upscale the production of these materials (Thostenson, et al, 2001; Couteau, et al, 2003; Goddard, et al, 2003; Kathyayini, et al, 2004; Li, et al, 2005; Iyuke et al, 2007; Abdulkareem et al, 2007; Afolabi et al, 2007). Good selectivity, flexibility and simplicity also favour the choice of CCVD and SFCCVD as the most frequently employed methods for carbon nanoparticles synthesis (Kathyayini, et al, 2004 and Seong, et al, 2005).

There is little difference between the CVD/SFCCVD methods of carbon nanotube synthesis and the conventional vapour grown technology of carbon nanotubes and carbon fiber synthesis. The CVD/SFCCVD methodology of producing carbon nanoballs emerged from the improvement and optimization of the conventional method of carbon nanotube production (Maragoni et al, 2001; Xu et al, 2005; Kim et al, 2005; Edgar and Spencer, 2006). In CVD and SFCCVD, carbon nanoballs can be grown from the decomposition of hydrocarbon, such as benzene, acetylene, ethane etc. over a metal catalyst in a temperature range of 500 to 900°C (Colomer et al, 2000; Li et al, 2004; Liu et al, 2004; Bartsch and Leonhardt, 2004; Gulino et al, 2005; Louis et al, 2005; Iyuke et

al, 2007; Afolabi et al, 2007). This method generates mixtures of randomly distributed carbon nanoballs in addition to graphitic filament and amorphous carbon with a wide variety of diameters (Kuwana and Saito, 2005; Mohlala, 2005; Monthieux et al, 2006). The mechanism of carbon nanoballs growth by the CVD and SFCCVD methods involves the growth of the CNBs on substrate such as carbon, silicon, etc., or on floating fine catalyst particles, e.g. Fe, Ni, Co or a mixture of the catalyst particles to form a bimetallic catalyst (Singh et al, 2003; Zhu et al, 2003). A typical catalytic chemical vapour deposition system shown in Figure 2.11 consists of a horizontal tube, 30 mm in diameter and 1000 mm in length (Xu et al, 2005; Kim et al, 2005; Edgar et al, 2006). The catalyst and carbon source are transported by the argon, hydrogen or mixture of both to the reaction chamber to form the nanostructure (Iyuke et al, 2006; Abdulkareem et al, 2007; Iyuke et al, 2007). The growth of the nanostructure occurs either in the heating zone, before or after the heating zone (Iyuke et al, 2007). The major advantage of the catalytic vapour deposition technique is the considerable reduction of amorphous carbon, the absence of graphite and high yield of carbon nanotubes (Seong et al, 2005).

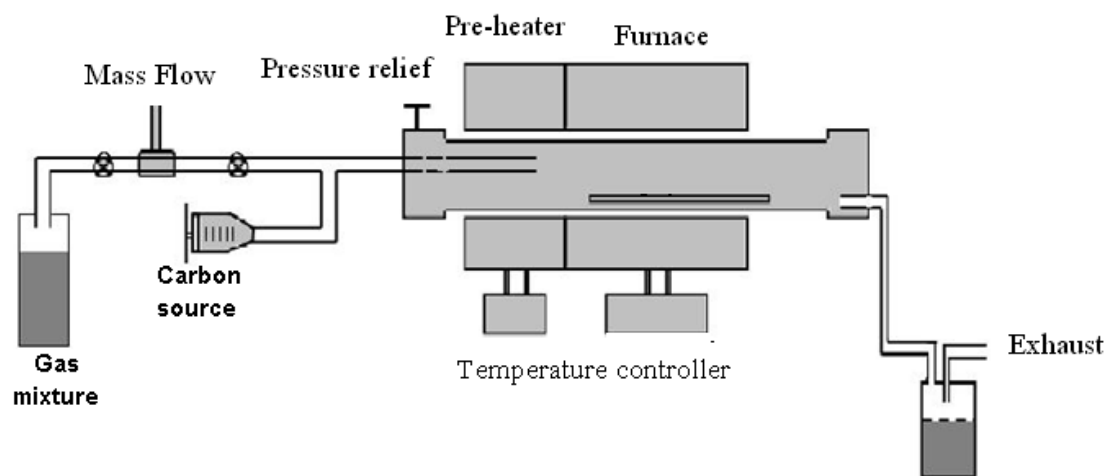


Figure 2.14: Chemical catalytic vapour deposition equipment

2.6.1 Characterization of Carbon Nanoballs

Carbon nanoparticles are usually black powder; the structure, quality and types of nanoparticles produced can only be identified by characterization. Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Thermo Gravimetric Analysis (TGA), X – ray diffractometer (XRD), Raman spectroscopy and BET were used to characterize carbon nanoballs.

Electron microscopy is an incredible tool for material characterization because it allows the examination of micro structural features of a material via high resolution imaging, and at the same time enables the acquisition of both the crystallographic and chemical information of the samples. Electron microscopy also has an increase in depth of field when compared to optical microscopy. This allows the electron microscope to give a clear picture of complicated topological features of a specimen. Therefore, the Transmission Electron Microscope and Scanning Electron Microscope are used to characterize the carbon nanoparticle samples, and in particular to verify their yield, wall structure and purity. TEM is regarded as the highest resolution imaging technique; it therefore gives useful information about the carbon nanoparticles. Information on the diameter, defects in nanoparticles and presence of amorphous carbon in the sample material can be obtained through the use of high-resolution TEM. Using the Scanning Electron Microscope with two maneuverable manipulations saves labour, time and reduces the probability of ‘trial and error’ during the manipulation; in addition it can be applied in any type of interconnection between nanostructure material and macro structured material (*Magazine of nanotechnology*, 2005). Electron microscopy is therefore a powerful technique for understanding the microstructure, structural defects and structural interface of carbon nanoparticles. Along with electron microscopy is

Raman scattering microscopy, which is probably the most commonly used equipment to characterize carbon nanoparticles. It gives information on types of carbon nanoparticles, their degree of crystallinity, diameter and also purity. The XRD, on the other hand, gives information on the composition of nanoparticles. The thermo gravimetric analysis is used in the presence of atmospheric nitrogen or air to monitor the weight loss of the catalyst at the temperature of catalytic vapour deposition, the thermal stability of purified samples and amount of functional covalently attached to the side walls of the carbon nanotubes. BET gives information on the pore volume, surface area and the chem.-sorption properties of nanoparticles.