1 Introduction

1.1 Fuel Cells for Energy Conversion

Successful energy conversion has been turning point in the human civilization. Over thousands of years, humanity has discovered and invented several conversion paths to satisfy the energy requirements. Each new form of energy conversion provided the opportunity to change the way of life dramatically. The simplest of such paths has been combustion, were primarily wood was burned for heating and cooking purposes. There are regions in the world where this practice continues until today. With the discovery of better fuels such as coal and oil, combustion remains an all-important path for harnessing energy. The development in electrical applications has however replaced many of the combustion-based applications. In the last hundred years, electrical energy has risen to be the most convenient and reliable source to power devices.

However, electrical energy mostly supplied by large power plants where the primary fuel is coal or oil, is obtained via a series of inefficient conversion paths. The chemical energy stored in these fuels is first converted to thermal energy via combustion. This energy is then converted to mechanical energy, which is finally converted to electrical energy. With each conversion path, the efficiency reduces drastically. The realization of limited natural resources as well as the environmental impacts of combustion of fossil fuels has been a huge motivation to look at alternate conversion paths. Fuel cell provides one such possibility to efficiently convert the stored chemical energy of fuels into electrical energy. Basic functioning of a fuel cell entails separating two chemical reactions, where in one reaction, electrons are donated and in the other, the electrons are accepted. The flow of the electrons from one side to another initiates the current which is used to power electrical devices. The mechanism is very similar to an electrochemical cell more commonly known as battery, with the exception that a battery is a energy storage system. A fuel cell on the other hand is used as a conversion system, which is dependent on supply of the necessary fuels.

The fuel cell concept is used for a variety of fuels and separating materials. Most commonly known fuel cells use a polymer electrolyte membrane (PEM) as a separator. This membrane is sandwiched between catalyst layers (anode and cathode) where the reactions take place. The typical fuels used in this system are hydrogen or methanol on the anode side and oxygen or air on the cathode side. The typical operating temperatures are in the range of 70°C to 90°C and the byproducts are usually water (in case of hydrogen) and carbon dioxide (in case of methanol). Such fuel cell systems are relatively easy to fabricate and operate. However, in order to increase the efficiency at the operating temperatures, catalyst metals such as platinum and ruthenium are necessary to catalyze the reactions. This increases the cost of fabrication and the operation is quite sensitive to catalyst degradation.

Other well known fuel cell types are the solid oxide fuel cell (SOFC) and the molten carbonate fuel cell (MCFC). These two fuel cell types operate at much higher temperature ranges of 600°C to 1000°C. The SOFC contains a solid ceramic separator and whereas the MCFC has a molten carbonate salt mixture suspended in porous ceramic matrix. High operating temperatures make it possible to use internal (or external) reformation of a wide variety of fossil fuels for providing hydrogen as the anode side fuel. Oxygen or air is used as the fuel on the cathode side. These two fuel cell types are mostly bulky and need a much longer start up time. They are largely used for stationary applications and the setup is technically challenging.

1.2 Fuel Cells for Automotive Applications

The automobile industry, like most other industries is headed towards efficient and environment friendly fuel consumption. With rising concerns of air pollution and global warming, low emission cars are generating quite an interest in both the populace and the governments the world over. The global dependence on the depleting oil resources adds to the motivation not only to reduce the fuel consumption but also to introduce alternative fuels for powering mobility.

Introduction of alternative fuels for the conventional combustion engines have not been entirely successful so far. Production of biomass based fuels such as ethanol, bio-diesel, etc. has been widely criticized for exerting undue pressure on the competing food grain production for human consumption. Controversies over the actual carbon dioxide compensation by such methods have also prevented worldwide acceptance for bio-fuels. Other alternatives such as natural gas or petroleum gas are feasible alternatives for combustion engines. Nevertheless, they are neither a renewable resource nor are they emission neutral.

A promising alternative to combustion powertrains is the electric mobility. Electric engines use any form of electrical energy for mobility and can theoretically circumvent the polluting and inefficient combustion stage of the energy conversion in case of conventional fuels. For example, solar energy can be directly harvested by solar or photovoltaic cells to produce electricity. Unfortunately, solar energy powered cars are largely limited by clear sunny skies and the capacity of the solar cells in energy conversion and therefore unfit for reliable mobility. However, renewable energy sources such as solar or wind power, can be used to store the electric energy in form of chemical energy and later be reused to power electric engines in cars. Electrochemical systems such as batteries and fuel cells make it possible for such an energy conversion path. And this provides the best scenario towards mobility with zero emission as well as independence from fossil fuels.

Battery is essentially an array of electrochemical cells that store and convert chemical energy into electrical energy. With the advances in the last few decades, the capacity of energy storage in batteries has increased by manifolds and made it a feasible candidate for powering electric cars. Also the latest lithium (Li) ion technology provides fast and multiple charging and discharging capabilities that make it ideal for automotive applications. Despite the obvious advantages of battery powered electric mobility, certain factors in comparison to the conventional cars are detrimental to its widespread acceptance in the markets. The two most important disadvantages of the battery are energy density and cost. A rough comparison with one of the available electric cars [Mitsubishi i MiEV] in the market show that they can manage only about 20 percent of the cruising range when compared to a similar sized car powered by a conventional internal combustion engine (ICE). The battery alone in such a car would cost as much as a conventional car. Mass production of such batteries could bring down the costs drastically but the energy density would always limit the cruising range to roughly 150 km per charging cycle. Among other operational issues, the time of recharging a discharged battery can run into a few hours making it unavailable for longer periods. Also the ageing of a battery is largely accelerated when charged or discharged incorrectly.

In contrast to batteries that store chemical energy, fuel cells are energy converters. An operational fuel cell needs constant supply of fuel. Therefore, the cruising range of a fuel cell powered electric car can be simply determined by the amount of stored fuel. The most feasible fuel cell system uses hydrogen and oxygen as fuels due to practical feasibility and high system efficiency and releases water and heat as products. Hydrogen is required to be stored in tanks whereas oxygen is sufficiently available from air. Also refueling of the hydrogen storage tanks can be accomplished in about 5 to 10 minutes. Currently the cost of a fuel cell system in prototype cars is also prohibitively high but technological advances and mass production could see a reduction in the costs to affordable ranges in the near future.

Due to the weight and operating temperatures, the high temperature fuel cells are not suited for direct automotive applications. Nevertheless, some efforts are being made to utilize the efficiency and the capability of SOFC to use fossil fuels for example, as auxiliary power units or APUs for large vehicles like trucks. In long idle modes, these heavy vehicles need power that is usually supplied via the combustion engine. This leads to extremely inefficient usage of the diesel over long periods. With the aid of the APUs, main combustion engine of the vehicle can be shut down and the diesel can be redirected to a reformer in the SOFC. The fuel cell can then take over the entire electrical demand of the vehicle in a more efficient manner. This greatly reduces both the fuel consumption as well as pollutant emissions. This concept is quite promising but faces quite some technical challenges such as space requirements of the APU, start up time and operating temperatures among others. Polymer electrolyte membrane based fuel cells are also being introduced as possible APU candidates. Companies are already marketing compact DMFCs for powering small camping wagons. All electrical needs of a small vehicle can be satisfied by such a system.

For the fuel cell system to replace the combustion engine presents an entirely different scenario. The system needs to be optimal in size, weight, operation and power. The hydrogen fueled PEM fuel cells are the ideal candidates for such an application. The fuel cell stack is relatively compact and delivers sufficient power for the vehicle drive train. The operating temperatures between 80°C and 160°C are suitable for quick starts and cooling requirements. The fuel tank in a conventional car is replaced by the hydrogen tanks. Fuel cell driven cars are already being introduced in small numbers in the markets where sufficient hydrogen infrastructure exists. Early reports show the feasibility of such a concept for regular use and of course the challenges that need to be overcome in the near future. In order to improve or resolve the disadvantages of the PEM fuel cell system, one needs to first understand the functioning of such a fuel cell. The following section introduces the basic functioning of one such type of fuel cell consisting of a polymer electrolyte membrane (PEM), which best suits the requirements of the automotive industry.

1.3 Fundamentals of Polymer Electrolyte Membrane Fuel Cells

A polymer electrolyte membrane fuel cell consists of two electrodes namely, the anode and the cathode separated by a polymer membrane. This is more commonly known as the membrane electrode assembly (MEA). The electrodes consist of carbon supported platinum particles that improve the electrochemical reaction rate. The hydrogen to the anode side and oxygen or rather air to the cathode side is supplied via flow field channels. The reactant gases then diffuse through a gas diffusion layer (GDL) usually consisting of carbon fibers to the catalyst layer where the reaction takes place. On the cathode side, the product gases are then transported out of the cell. An overview is depicted in Fig. 1.1.

On the anode side, hydrogen molecules dissociate on platinum catalyst to form protons and electrons causing a charge surplus. The protons are transported through the polymer membrane to the cathode side where they reduce the oxygen molecules creating a charge deficit. This creates the potential difference between the two electrodes and under a given load, makes the electron flow through an external circuit to the cathode. On the cathode side the migrated protons react with the oxygen molecules on platinum catalyst along with the conducted electrons to produce water. This water diffuses out through the GDL and leaves the system through the flow channels.

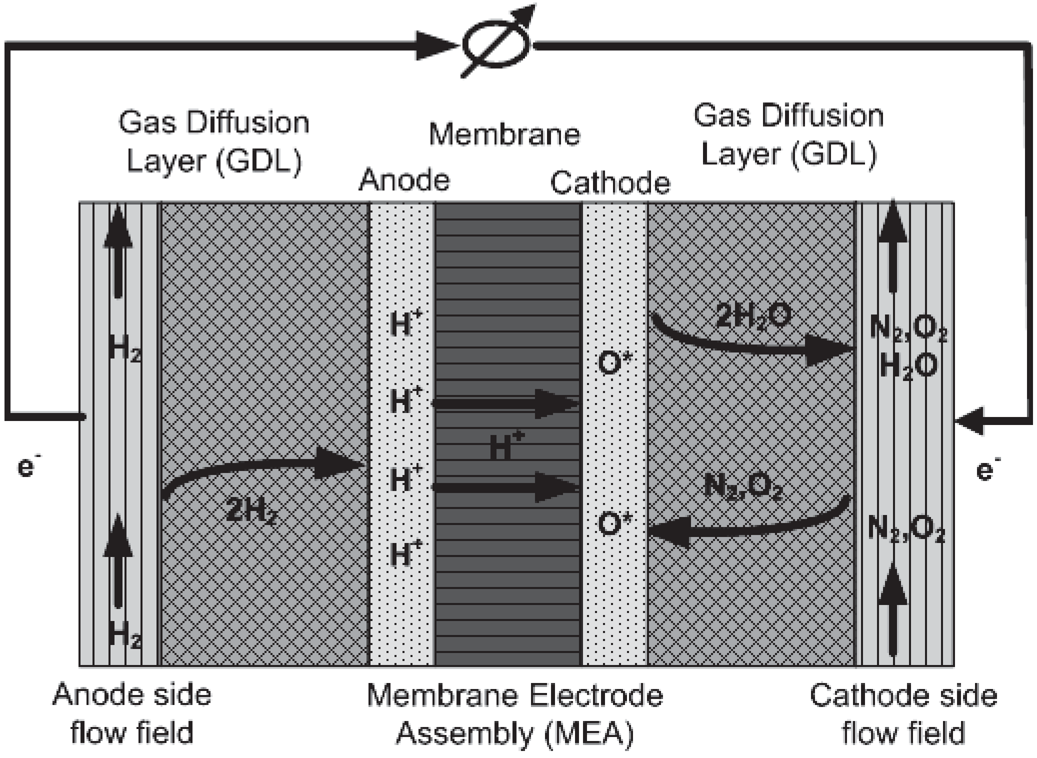

Figure 1.1: Schematic description of the working principle of a PEM fuel cell

The proper functioning of the PEM is the key to reliable fuel cell operation. The most commonly used membrane is called Nafion®, which was developed by a chemical company DuPont. It is a sulfonated tetrafluroethylene based fluoropolymer-copolymer. This membrane is an excellent proton conductor while acting as an insulator for electrons and anions. Also it exhibits very low permeability to reactant gases. In fuel cell operation, the solid polymer membrane is coated with catalyst particles and then humidified with water that fills up the porous membrane structure. The proton transport through the membrane is carried out by three parallel mechanisms. The protons on the sulfonic acid groups hop from one site to another also referred to as surface hopping. Some protons are transported via diffusion as solvated protons with water molecules. Third and the most effective mechanism is the proton hopping in the fluid media. Here, the positive charge of the proton diffuses through the network of water molecules. Water plays an essential role in the functioning of this fuel cell. Low humidification is detrimental to proton conductivity and mechanical stability of the membrane. This limits the operating temperatures to well under 100°C (typically 80°C). At such low operating temperatures the platinum particles are extremely sensitive to catalyst poisoning as well as limit the overall fuel cell reaction rate. An extremely high purity of fuel gases, particularly hydrogen is required to avoid loss due to catalyst poisoning. Therefore, a Nafion® based fuel cell system at low temperatures (less than 100°C) presents certain fundamental restrictions towards further improvement in performance. Water management is seen to be the biggest challenge for reliable fuel cell operations with an external humidification unit as an essential support. Flooding of the GDL with water is always a possibility, which usually blocks the fuel gas transport to the catalyst layer. Increase in operational temperature is thus very favorable since the water transport in the GDL will then be in gaseous phase and the catalyst activity as well as resistance will be considerably enhanced. This is however not possible in the existing setup since the Nafion® membrane is structurally unstable at higher temperatures.

A fuel cell based on polybenzimidazole (PBI) membrane is a promising alternative to Nafion® based fuel cells. The PBI membrane is doped with phosphoric acid that acts as a medium for proton transport. All other components and operations of the fuel cells are quite similar to the one described before. Such a membrane exhibits reasonable proton conductivity via two mechanisms at higher operating temperatures of up to 300°C. Protons conduction is by a combination of Grotthus mechanism (similar to proton hopping) and diffusion along with the phosphoric acid moieties. Typical operating temperature of such fuel cell can be up to 200°C where all product water is in the gas phase and therefore easily transported out of the system. Furthermore, at these temperatures, the platinum particles are quite resistant to fuel impurities and reaction rates are relatively high. Such a fuel cell system is an ideal candidate for utilizing slightly impure hydrogen gas obtained from onboard reformation of fossil fuels or bio-fuels. These characteristics of the high temperature (HT) PEM fuel cell promise a simpler system by avoiding water management components and better catalyst stability.

1.4 Principle

The electrochemical reaction occurring in a fuel cell is fundamental to its performance. The overall reaction in the HT PEM fuel cell is essentially the hydrogen reaction with oxygen to produce water.

$$\mathrm{2H_2 + O_2 \rightarrow 2H_2O} \tag{1.1}$$

The hydrogen supplied on the anode side flow field diffuses through the GDL and dissociates on the platinum catalyst. A single hydrogen molecule accounts for two protons and two electrons. The protons migrate to the cathode side through the PBI membrane and the electrons flow under a given load to the cathode by an external circuit.

$$\mathrm{H_2 \rightarrow 2H^+ + 2e^-} \tag{1.2}$$

On the cathode side, air is supplied via the flow fields into the fuel cell. Oxygen diffuses through the GDL and adsorbs on the catalyst surface. These molecules then react with protons and electrons to produce water. The product water desorbs from the platinum surface and diffuses out of the cell.

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \tag{1.3}$$

Both the anode as well as cathode reactions have their respective reaction rates. The hydrogen oxidation reaction (HOR) on the anode side is much faster than the cathode side oxygen reduction reaction (ORR). Therefore the overall cell reaction rate is limited by the ORR and can be written as

$$r = k_{ORR}\, C_{O_2}\, C_{H^+}\, \theta_{\mathrm{Pt}}\, f(U) \tag{1.4}$$

The reaction rate is the product of the oxidation reaction rate constant, concentration of oxygen and protons available for reaction, the available active platinum catalyst sites and a cell potential dependent function. Fundamental limitations on the HT PEM fuel cell