

Introduction to Fuel Cell Technology

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May 2, 2003

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Chapter 1

Preface

This document was produced for a directed reading class at the University of Notre Dame. The class was a result of two students, Chris Rayment and Scott Sherwin, who were interested in learning about fuel cells and two professors, Mihir Sen and Paul McGinn, who agreed to conduct the course.

The course consisted of weekly presentations on the written chapters. This report is a result of each weekly presentation. The course outline was determined by us, Chris and Scott, and evenly distributed between the two of us. The first half of the course consisted of an introduction into fuel cells and the various types whereas the second half of the course consisted of applications and current research in the fuel cell field. This is representative of the general layout of the report.

The goal of this report was to produce a document showing our work for the semester and also to make available to other students interested in fuel cells or taking an introductory fuel cell course.

We would like to thank Professor Mihir Sen and Professor Paul McGinn from the University of Notre Dame for their time and guidance in conducting this course. Their knowledge and experience in Engineering was greatly beneficial to the success of this course and thus the report. Chris Rayment Scott Sherwin ©Chris Rayment and Scott Sherwin

Chapter 2

Introduction

2.1 Fuel Cell Basics

A fuel cell is a device that uses hydrogen as a fuel to produce electrons, protons, heat and water. Fuel cell technology is based upon the simple combustion reaction given in Eq. (2.1):



The electrons can be harnessed to provide electricity in a consumable form through a simple circuit with a load. Problems arise when simple fuel cells are constructed. Simple fuel cells have a very small area of contact between the electrolyte, the electrode, and the gas fuel. Simple fuel cells also have high resistance through the electrolyte as a result of the distance between the electrodes.

Therefore, as a result of these problems, fuel cells have been designed to avoid them. A design solution includes manufacturing a flat plate for the electrodes with an electrolyte of very small thickness between the two electrodes. A very porous electrode with a spherical microstructure is optimal so that penetration by the electrolyte and gas can occur. This design gives the maximum area of contact between the electrodes, electrolyte and gas thus increasing the efficiency and current of the fuel cell.

A fuel cell does not require recharging the same as a battery. In theory a fuel cell will produce electricity as long as fuel is constantly supplied. The basic design of a fuel cell involves two electrodes on either side of an electrolyte. Hydrogen and oxygen pass over each of the electrodes and through means of a chemical reaction, electricity, heat and water are produced.

Hydrogen fuel is supplied to the anode (negative terminal) of the fuel cell while oxygen is supplied to the cathode (positive terminal) of the fuel cell. Through a

chemical reaction, the hydrogen is split into an electron and a proton. Each takes a different path to the cathode. The electrons are capable of taking a path other than through the electrolyte, which, when harnessed correctly can produce electricity for a given load. The proton passes through the electrolyte and both are reunited at the cathode. The electron, proton, and oxygen combine to form the harmless byproduct of water. This process is shown in Fig. 2.1.

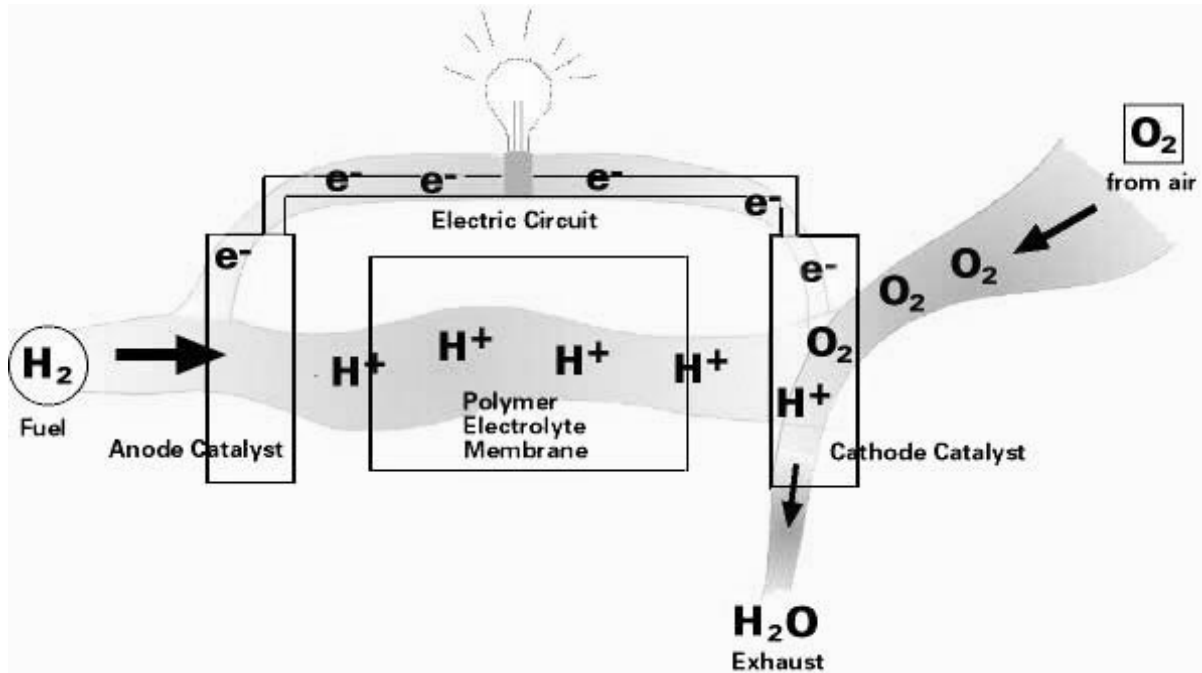


Figure 2.1: Basic Fuel Cell Operation

The hydrogen fuel can be supplied from a variety of substances if a “fuel reformer” is added to the fuel cell system. Therefore, hydrogen can be obtained from hydrocarbon fuel such as natural gas or methanol. The fuel cell’s means for producing electricity is through a chemical reaction, therefore there are significantly cleaner emissions than from a fuel combustion process.

2.2 History of Fuel Cell Technology

The origin of fuel cell technology is credited to **Sir William Robert Grove** (1811-1896). Grove was educated at Oxford and practiced patent law while also studying chemistry. Grove developed an improved wet-cell battery in 1838 which brought him

fame. Using his research and knowledge that electrolysis used electricity to split water into hydrogen and oxygen he concluded that the opposite reaction must be capable of producing electricity. Using this hypothesis, Grove developed a device which would combine hydrogen and oxygen to produce electricity. Grove had developed the world's first gas battery. It was this gas battery which has become known as the fuel cell.

Ludwig Mond (1839-1909) along with assistant Carl Langer conducted experiments with a hydrogen fuel cell that produced 6 amps per square foot at 0.73 volts. Mond and Langer came across problems using liquid electrolytes. As Mond said "we have only succeeded by using an electrolyte in a quasi-solid form soaked up by a porous non-conducting material, in a similar way as has been done in the so-called dry piles and batteries." Mond used an earthenware plate saturated with dilute sulfuric acid.

It was **Friedrich Wilhelm Ostwald** (1853-1932), the founder of the field of physical chemistry, who experimentally determined the relationship between the different components of the fuel cell, including the electrodes, electrolyte, oxidizing and reducing agent, anions and cations. Ostwald's work opened doors into the area of fuel cell research by supplying information to future fuel cell researchers.

During the first half of the twentieth century, **Emil Baur** (1873-1944) conducted extensive research into the area of high temperature fuel cell devices which used molten silver as the electrolyte. His work was performed along with students at Braunschweig and Zurich.

Francis Thomas Bacon (1904-1992) performed research and significant developments with high pressure fuel cells. Bacon was successful in developing a fuel cell that used nickel gauze electrodes and operated at pressures up to 3000 *psi*. Bacon's work lead into World War II as he tried to develop a fuel cell to be used in the Royal Navy submarines. In 1958, his work lead to the development of an alkali cell using a stack of 10" diameter electrodes for Britain's National Research Development Corporation. Bacon's developments were successful enough gain the interest of Pratt & Whitney, and his work was licensed and used in the Apollo spacecraft fuel cells. Similar technology is still being used in spacecraft.

2.3 Why are we studying Fuel Cells?

Currently there is a lot of active research throughout the world on solving engineering problems that currently prevent fuel cells from becoming commercially available. Some of these current problems are the high initial cost of manufacturing the fuel cell, the lack of an infrastructure to deliver fuels to the cells, and the unfamiliarity that the industry has with the fuel cell.[13] These problems highlight three areas. First the industry must reduce the cost of producing fuel cells; these problems are mainly

engineering or manufacturing problems associated with each type of fuel cell. The second issue is one of policy and engineering. In order to develop an infrastructure for fuel cells first a specific type of fuel cell needs to be chosen so the infrastructure can correctly be developed to support the specific needs of the cell. Also there needs to be several policy changes that can account for the new source of electric power, i.e. standardization, safety codes, and regulations for production of the fuels and the distribution of the fuels. The final noted hurdle that must be solved before commercialization can begin is the power industry needs to be familiarized with this emerging technology. This education of the industry will occur over time as the technology becomes more commonplace as a form of energy generation and as the power companies themselves move toward a more hydrogen based form of electric power generation. Thus as an introduction to fuel cells we need to study cell cells for two important reasons. First they are an emerging technology that needs to be understood, thus enabling the continuation of R & D and the eventual rollout of commercialization. Secondly we need to study fuel cells because we need to learn how the presence of fuel cells will change current application of energy dependent devices.

2.3.1 Why Fuel Cells are an Emerging Technology

As mentioned above the major disadvantage of the fuel cell is that it is currently more expensive than other forms of power conversion. But this is a barrier that is soon to be broken. Previously the application of fuel cells was purely for use in niche applications like the space shuttles of the 60's. But as R&D has progressed in the past 40 years the cost of the fuel cell has dropped dramatically, the current cost is about \$1,500/kW. According to most research analysts the necessary cost that producers must reach is around the \$400/kW range. To address this cost barrier the government has awarded \$350 million in research grants to several companies to lower the initial cost of the cell to the necessary price range. The government is working in this area through a branch organization of the Department of Energy, called the Solid State Energy Conversion Alliance (SECA). The SECA has distributed money and provided help to four major companies in an effort to break the cost barrier by the year 2010. Once this barrier is broken it is widely speculated that fuel cells will become a dominant source of energy conversion. The reason for their desirability is that they are extremely efficient, simple, have virtually no emissions, and they run silent.[9] Current fuel cells, when operated alone have efficiencies of about 40%-55%, and when they are used with CHP they can reach efficiencies of 80%.[13] This is a dramatic improvement over a current internal combustion engine which is limited to an efficiency of about 30%. The simplistic design of fuel cells will contribute greatly to their longevity. They have virtually no moving parts, and in some cases are made entirely of solids. This not only simplifies the manufacturing process but

it also will allow the cells to have longer operational periods. Since the output of an ideal fuel cell is pure water, the emissions are extremely low. Depending on the type of fuel cell and the fuel used the actual emissions of fuel cells fall well below any current standard of emissions. If the fuel cell is applied to the L.A Basin emissions requirements we find that it falls well below the maximums. It emits <1ppm of NO_x, 4ppm of CO, and <1ppm of reactive organic gases, while the standards are an order of magnitude greater for NO_x, two orders of magnitude greater for reactive organic gases, and several orders of magnitude larger for CO. The final advantage of the fuel cell that many consumers will appreciate is the silence of operation. The cell converts energy through a chemical process, as opposed to a mechanical process like in an internal combustion engine, thus the sound emissions are virtually zero. This is important especially in onsite applications and in vehicle application. All of these major advantages make fuel cells an excellent choice of the future of power generation.

2.3.2 What are the applications of Fuel Cells?

The applications of fuel cells vary depending on the type of fuel cell to be used. Since fuel cells are capable of producing power anywhere in the 1 Watt to 10 Megawatt range they can be applied to almost any application that requires power. On the smaller scale they can be used in cell phones, personal computers, and any other type of personal electronic equipment. In the 1kW - 100kW range a fuel cell can be used to power vehicles, both domestic and military, public transportation is also a target area for fuel cell application, along with any APU application. And finally, in the 1MW - 10MW range fuel cells can be used to convert energy for distributed power uses (grid quality AC).[9] Since fuel cells can be used anywhere in the power spectrum their development will have an immediate impact in their prospective power range. One of the major applications for the fuel cell in the future will likely be that of domestic and public transportation. The fuel cell is well adapted to this application because use of a fuel cell will reduce the design complexity of a vehicle. Currently GM has devoted a lot of their future planning on the incorporation of the fuel cell in their designs. They would like to create a drive-by-wire vehicle that would remove the dependence of today's cars on mechanical systems. This conversion to a totally electronic vehicle would greatly reduce the number of moving parts in the car, thus dramatically decreasing the likelihood of failure. In the low scale range the fuel cell has a great advantage over batteries in that they do not need to be recharged, only fueled, and they have much higher power densities than current commercialized batteries. Since they can provide more power per area the cell can be smaller while applying the same power, thus saving space considerably. In a large scale setting the fuel cell can be used to assist in increasing the efficiency of the current turbine power plant. By using the hot exhaust from the fuel cell and transferring it to a turbine

power cycle the overall practical efficiency of the system can reach up to 80%.

Part I

Fuel Cell Basics and Types

Chapter 3

Open Circuit Voltage and Efficiency

3.1 Open Circuit Voltage

Fuel cell efficiency can not be analyzed the same as a thermodynamic system using the Carnot efficiency. Unlike many electrical power generating systems it is not obvious what form of energy is being converted into electricity in a fuel cell. The inputs and outputs of the basic fuel cell are shown in Fig. 3.1.

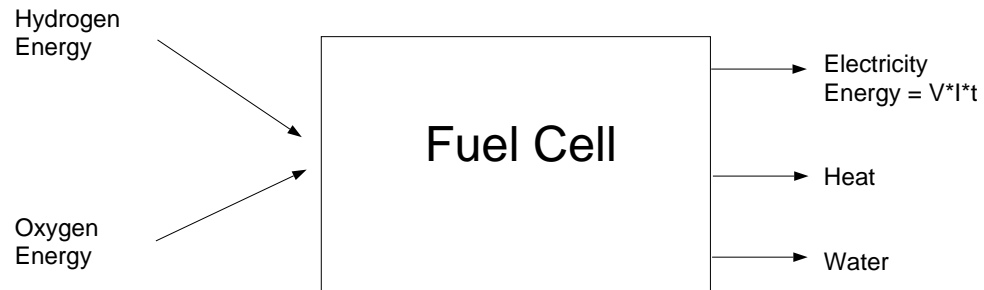


Figure 3.1: Basic Fuel Cell Inputs and Outputs

The power and energy is the same as that for any electrical system.

$$Power = VI \quad \text{and} \quad Energy = Power \times t = VIt \quad (3.1)$$

To analyze the chemical energy changes throughout the chemical process involved in the operation of a fuel cell, one must be aware of and understand “Gibbs free energy.” This is defined as the “energy available to do external work, neglecting

any work done by changes in pressure and/or volume.” [9] A simple analogy can be made between “chemical energy” and “potential energy.” Just as for potential energy, chemical energy has reference points from which all other system chemical states are based upon. For chemical energy the *point of zero energy can be define as almost anywhere*. “Gibbs free energy of formation”, G_f is used when this convention is used. Therefore, the Gibbs free energy of formation is zero for the input state, thus simplifying calculations and creating a standard. The Gibbs function of formation is defined below:

$$\bar{g} = \bar{h} - T\bar{s} \quad (3.2)$$

where \bar{h} is enthalpy per mole, T is temperature, and \bar{s} is entropy per mole.

The Gibbs function at a state other than the standard state is found by adding the Gibbs free energy of the standard state with that of the specific Gibbs function of the state of interest as expressed below:

$$\begin{aligned} \bar{g}(T, p) &= \bar{g}_f^o + [\bar{g}(T, p) - \bar{g}(T_{ref}, p_{ref})] \\ &= \bar{g}_f^o + \Delta\bar{g} \end{aligned} \quad (3.3)$$

where \bar{g}_f^o is the absolute Gibbs energy at $25^\circ C$ and 1 atm. Applying Eq. (3.2) to Eq. (3.3) we obtain the equation below:

$$\Delta\bar{g} = [\bar{h}(T, p) - \bar{h}(T_{ref}, p_{ref})] - [T\bar{s}(T, p) - T_{ref}\bar{s}(T_{ref}, p_{ref})] \quad (3.4)$$

Enthalpy in Eq. (3.2) is defined as:

$$\bar{h} = \bar{u} + p\bar{v} \quad (3.5)$$

where \bar{u} is the specific internal energy per mole, p is pressure, and \bar{v} is the specific volume. Entropy is defined as:

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T} \right)_{IntRev} \quad (3.6)$$

where δQ is the heat transfer at a part of the system boundary during a portion of the cycle, and T is the temperature. Assuming ideal gas behavior entropy at any temperature and pressure is determined by:

$$\bar{s} = \bar{s}(T, p_{ref}) + [\bar{s}(T, p) - \bar{s}(T, p_{ref})] \quad (3.7)$$

which can be expanded to:

$$\bar{s}(T, p) = \bar{s}^o(T) - \bar{R} \ln \left(\frac{p}{p_{ref}} \right) \quad (3.8)$$

where \bar{s}^o is the absolute entropy at temperature T and pressure p . The absolute entropy is defined as:

$$\bar{s}^o(T) = \int_0^T \frac{c_p(T)}{T} dT \quad (3.9)$$

Also just the same as potential energy can change, chemical energy can also change; therefore, it is useful to calculate the change in Gibbs free energy of formation, or ΔG_f . This change determines the energy released during the chemical process. The change is defined as follows in Eq. (3.10):

$$\Delta G_f = G_f \text{ of products} - G_f \text{ of reactants} \quad (3.10)$$

A much more common and useful notation is the Gibbs free energy of formation in the “per mole” form. Using the correct notation for the “per mole” form, Eq. (3.11) then becomes:

$$\Delta \bar{g}_f = \bar{g}_f \text{ of products} - \bar{g}_f \text{ of reactants} \quad (3.11)$$

Applying the previous equations to the basic simple combustion equation presented in Ch.1:



equivalent to:



Therefore, applying Eq. (3.11), we have:

$$\Delta \bar{g}_f = (\bar{g}_f)_{H_2O} - (\bar{g}_f)_{H_2} - \frac{1}{2}(\bar{g}_f)_{O_2} \quad (3.14)$$

Difficulty in the above equation comes because the “Gibbs free energy” is not constant but varies with both temperature and the products state. Table 3.1 shows $\Delta \bar{g}_f$ for various temperatures and states.

Assuming Eq. (3.13) is reversible, meaning that all the Gibbs free energy is converted into electrical energy, then the Gibbs free energy can be used to find the open circuit voltage of the fuel cell. If we designate $-e$ as the charge on one electron, and knowing that two electrons are produced during the basic combustion reaction, then the charge that is produced by the reaction is:

$$-2 N e = -2F \text{ Coulombs} \quad (3.15)$$

where F is the Faraday constant which is the charge on one mole of electrons, and N is Avagadro’s number.

Form of water product	Temp °C	$\Delta\bar{g}_f$ kJ/mole	Max EMF	Efficiency limit
Liquid	25	-237.2	1.23V	83%
Liquid	80	-228.2	1.18V	80%
Gas	100	-225.3	1.17V	79%
Gas	200	-220.4	1.14V	77%
Gas	400	-210.3	1.09V	74%
Gas	600	-199.6	1.04V	70%
Gas	800	-188.6	0.98V	66%
Gas	1000	-177.4	0.92V	62%

Table 3.1: Gibbs free energy for water for various temperatures and states

The electrical work done by the fuel cell in moving two electrons around the circuit is given by Eq. (3.16):

$$\begin{aligned} \text{Electrical work done} &= \text{charge} \times \text{voltage} \\ &= -2FE \quad \text{Joules} \end{aligned} \quad (3.16)$$

where E is the voltage of the fuel cell.

Since the process is reversible then the electrical work done will be equal to the Gibbs free energy released, $\Delta\bar{g}_f$. Therefore, Eq. (3.15) becomes,

$$\Delta\bar{g}_f = -2FE \quad (3.17)$$

when rearranged, gives:

$$E = \frac{-\Delta\bar{g}_f}{2F} \quad (3.18)$$

where E is the EMF or reversible open circuit voltage for a hydrogen fuel cell.

3.2 Efficiency

The efficiency of a fuel cell is determined by the Gibbs free energy, $\Delta\bar{g}_f$, and the “enthalpy of formation”, $\Delta\bar{h}_f$. The “enthalpy of formation” is the value given to the heat that would be produced by burning the fuel. The “enthalpy of formation” is more commonly referred to as the “calorific value.” The efficiency of a fuel cell is given by:

$$\frac{\text{electrical energy produced per mole of fuel}}{-\Delta\bar{h}_f} = \frac{\Delta\bar{g}_f}{\Delta\bar{h}_f} \quad (3.19)$$

The efficiency equation, Eq. (3.19), can be ambiguous in that the enthalpy of formation, $\Delta\bar{h}_f$, depends on the state of the H_2O product in the governing combustion equation. The product H_2O can be in the form of either steam or liquid. For the product H_2O in the form of steam being produced, $\Delta\bar{h}_f = -241.83 \text{ kJ/mole}$, whereas, for H_2O in the form of liquid being produced, $\Delta\bar{h}_f = -285.84 \text{ kJ/mole}$. The difference in the two enthalpy of formation values is due to the molar enthalpy of vaporization of water. The enthalpy of formation, $\Delta\bar{h}_f = -285.84 \text{ kJ/mole}$, corresponding to the H_2O in the liquid state is known as the higher heating value (HHV). The enthalpy of formation, $\Delta\bar{h}_f = -241.83 \text{ kJ/mole}$, corresponding to the H_2O is known as the lower heating value (LHV). The heating value is a common term applied to a fuel, and it is a positive number equal to the enthalpy of combustion. The higher heating value is the value given when the product of the combustion is a liquid and the lower heating value is the value corresponding to when the product is in the gas form. The enthalpy of formation is easily calculated from the equation below:

$$\bar{h}_{RP} = \sum_P n_e(\bar{h}_f^o + \delta\bar{h})_e - \sum_R n_i(\bar{h}_f^o + \delta\bar{h})_i \quad (3.20)$$

where P and R correspond to the products and reactants, respectively, in any general combustion equation, n corresponds to the respective coefficients of the reaction equation giving the moles of reactants and products per mole of fuel, and \bar{h} is the enthalpy. Therefore, the maximum efficiency for a fuel cell is determined by Eq. (3.21):

$$\text{Maximum efficiency possible} = \frac{\Delta\bar{g}_f}{\Delta\bar{h}_f} \times 100\% \quad (3.21)$$

where the maximum efficiency of any system is the actual energy produced by the reaction, \bar{g}_f divided by the ideal energy produced by the reaction, \bar{h}_f . The Gibbs free energy, \bar{g}_f , is the actual energy produced by the combustion reaction, and the enthalpy of formation, \bar{h}_f , is the ideal energy that can be produced by the combustion reaction if the maximum energy was produced by the combustion reaction. Table 3.1 gives the value of maximum efficiency for a range of operating temperatures. Some interesting points about the efficiency of a fuel cell are [9]:

- Even though a fuel cell is more efficient at lower temperatures as shown in Table 3.1, the voltage losses are much less in higher temperature fuel cells. Therefore, it is more advantageous to run a fuel cell at a higher temperature yet lower efficiency to produce higher operating voltages.

- Fuel cells operating at higher temperatures will produce more heat which can be harnessed and used in a much more efficient manner than the low heat produced by low temperature fuel cells.
- Fuel cells do not necessarily have a higher efficiency than heat engines. A heat engine is actually more efficient at higher temperatures depending on the specific fuel cell being analyzed.

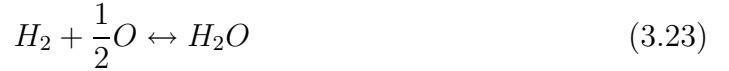
3.2.1 Efficiency Related to Pressure and Gas Concentration

The efficiency of a fuel cell is affected by more than just temperature. The pressure of the fuel and the gas concentration of the fuel is vitally important in the efficiency of the fuel cell.

In the case of any chemical reaction the products and reactants have an associated "activity." The activity is defined by:

$$\text{activity } a = \frac{P}{P^o} \quad (3.22)$$

where P is the partial pressure of the gas and P^o is the standard pressure, or 0.1 MPa . If we consider the hydrogen fuel cell reaction:



The activity of the products and reactants alters the Gibbs free energy equation. Applying Eq. (3.8) and Eq. (3.22) to Eq. (3.2) we obtain a new form of the Gibbs equation:

$$\Delta \bar{g}_f = \Delta \bar{g}_f^o - RT \ln \left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \quad (3.24)$$

where values for $\Delta \bar{g}_f^o$ are given in Table 3.1, and a_{H_2} , a_{H_2O} , and $a_{O_2}^{\frac{1}{2}}$ are the activation energies for the products and reactants.

The altered form of the Gibbs free energy equation given in Eq. (3.24) will affect the voltage of a fuel cell. Substituting Eq. (3.24) into Eq. (3.18) we obtain the "Nernst" equation:

$$E = \frac{-\Delta \bar{g}_f^o}{2F} + \frac{RT}{2F} \ln \left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right)$$

$$= E^0 + \frac{RT}{2F} \ln \left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \quad (3.25)$$

where E^0 is the EMF at standard pressure. The voltage given in Eq. (3.25) is known as “Nernst voltage.” Applying Eq. (3.22) to Eq. (3.25), assuming that the produced H_2O steam behaves as an ideal gas, and the pressures are given in bar, then Eq. (3.25) reduces to:

$$E = \frac{-\Delta \bar{g}_f^0}{2F} + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right) \quad (3.26)$$

If we use the relationships

$$\begin{aligned} P_{H_2} &= \alpha P \\ P_{O_2} &= \beta P \\ P_{H_2O} &= \delta P \end{aligned} \quad (3.27)$$

where P is the pressure of the system and α, β , and δ are constants that depend on the molar masses and concentrations of H_2, O_2 , and H_2O . Applying these relationships to Eq. (3.25) we obtain:

$$\begin{aligned} E &= E^0 + \frac{RT}{2F} \ln \left(\frac{\alpha \beta^{\frac{1}{2}}}{\delta} P^{\frac{1}{2}} \right) \\ E &= E^0 + \frac{RT}{2F} \ln \left(\frac{\alpha \beta^{\frac{1}{2}}}{\delta} \right) + \frac{RT}{4F} \ln(P) \end{aligned} \quad (3.28)$$

As we can observe from the different forms of the “Nernst” equation, there are many variables when considering the EMF of a fuel cell, which makes them very complex in analyzing and optimizing.

3.3 Nernst Equation Analysis

There are various ways of analyzing the different forms of the Nernst equations. The EMF is affected depending on the state and type of hydrogen supplied, be it in pure form or part of a mixture. The fuel and oxidant utilization and the system pressure affect the system EMF.

3.3.1 Hydrogen Partial Pressure

The voltage drop can be determined if we assume that P_{O_2} and P_{H_2O} are unchanged, and that the hydrogen partial pressure changes from P_1 to P_2 . Substituting the partial pressures, isolating the hydrogen term, and finding the difference in the EMF used in Eq. (3.28) we obtain the voltage drop which is:

$$\begin{aligned}\Delta V &= \frac{RT}{2F} \ln(P_2) - \frac{RT}{2F} \ln(P_1) \\ &= \frac{RT}{2F} \ln\left(\frac{P_2}{P_1}\right)\end{aligned}\tag{3.29}$$

A relevant example that has been tested in laboratory is the Phosphoric acid fuel cells with a temperature of $T = 200^\circ C$. Using Eq. (3.29) and substituting the proper values for R , T , and F we get:

$$\Delta V = 0.02 \ln\left(\frac{P_2}{P_1}\right) \quad \text{volts}\tag{3.30}$$

Comparing to experimental values by Hirschenhofer this voltage gives good agreement.[8] The experimental results were approximately 0.024 whereas we calculated 0.02. This correlation is affected by the concentration of hydrogen and therefore does not correlate as closely at differing concentration levels. The same arguments can be applied to the system pressure and various temperatures applied to Eq. (3.29).

3.3.2 Fuel and Oxidant Utilization

As the fuel cell is operating, oxygen is used and therefore the partial pressure of the oxygen will reduce. The partial pressure of the fuel decreases as the fuel is utilized in the fuel cell. As a result of conservation of mass, if oxygen and hydrogen are being used to produce H_2O then the partial pressure of H_2O should increase. Analyzing Eq. (3.28) in light of the change in partial pressure, it is clear that α and β decrease as δ increases. The change in partial pressures results in a smaller value of:

$$\frac{RT}{2F} \ln\left(\frac{\alpha\beta^{\frac{1}{2}}}{\delta}\right)\tag{3.31}$$

The result of the decrease in value is a decrease in EMF. This value varies throughout the fuel cell and the most losses are at the exit of the fuel cell where the fuel is being used.

3.3.3 System Pressure

As the Nernst equations show, Eq. (3.28), the EMF of the fuel cell will increase with an increase in system pressure, P , given by the following term:

$$\frac{RT}{4F} \ln(P) \quad (3.32)$$

Therefore a change in voltage will be obtained with a change in pressure from P_1 to P_2 as given by:

$$\Delta V = \frac{RT}{4F} \ln \left(\frac{P_2}{P_1} \right) \quad (3.33)$$

As we have shown, the voltage of a fuel cell is determined by the concentration of the reactants and the pressure of the fuel being supplied to the fuel cell.

Chapter 4

Causes for Voltage Loss

4.1 Introduction

The discussion of the last chapter was to derive the theoretical output voltage, EMF of a fuel cell. The EMF was approximately 1.2 Volts for a low temperature fuel cell (40 °C) and about 1 Volt for a high temperature fuel cell (800 °C). This voltage is never truly realized; sometimes it isn't even reached when the open circuit voltage is measured, as graph Fig. 4.1 shows. There are also some noticeable differences between Fig. 4.1 and Fig. 4.2. First, the high temperature graph does not display any large initial voltage loss, it also does not have any initial rapid fall in voltage, in the 0-100 $\frac{mA}{cm^2}$ range. In contrast the low temperature fuel cell loses .3 V at open circuit and another .2 V in the low current density range. Although these two fuel cells act very different at low current densities their graphs are very similar in character in the mid and high current density ranges. Both the low and high temperature fuel cells show a linear digression until they reach high current density. At this point both cells rapidly loose voltage with respect to increasing current density, this sudden fall in voltage occurs at about 900 $\frac{mA}{cm^2}$ in both the low and high temperature cells. Since the voltage of the cell is not seen as operating at the theoretically described EMF, we must now investigate the source of the losses in the system. We must modify the theoretical equation so that it models real life. This chapter will describe why there are voltage losses across the cathode and anode, and how these losses can be minimized.

4.1.1 Common Terminology

Since many different groups of people are interested in fuel cells, and the field of engineering has different terminology for similar ideas, it is important to understand the language as well as the engineering system. One of the areas that offer the most

confusion is the topic of voltage differentials. The first necessary term describing the voltage difference is “over voltage” or “over potential”. This is typically an electrochemists view of difference generated at the surface of an electrode. This voltage is superimposed over the ideal (reversible) voltage, but in the case of fuel cells the over voltage actually reduces the reversible voltage. Another common term that can be used is “irreversibility”. This term has its origins in thermodynamics. The way in which this term is often applied is to heat loss in a Carnot cycle, but in a fuel cell system due to the chemical conversion of energy the irreversibility’s are extremely low. [9]

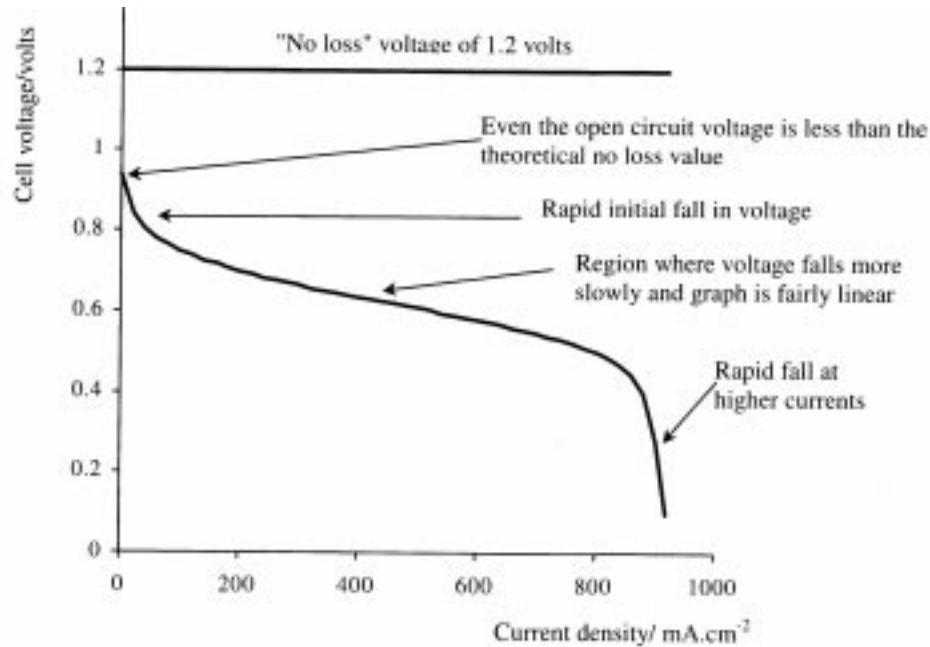


Figure 4.1: Low Temperature Fuel Cell Losses

4.2 General Voltage Loss Descriptions

4.2.1 Initial Theoretical Voltages

Last chapter showed the theoretical voltage of a fuel cell is derived to be:

$$E = \frac{-\Delta\bar{g}_f}{2F} \quad (4.1)$$

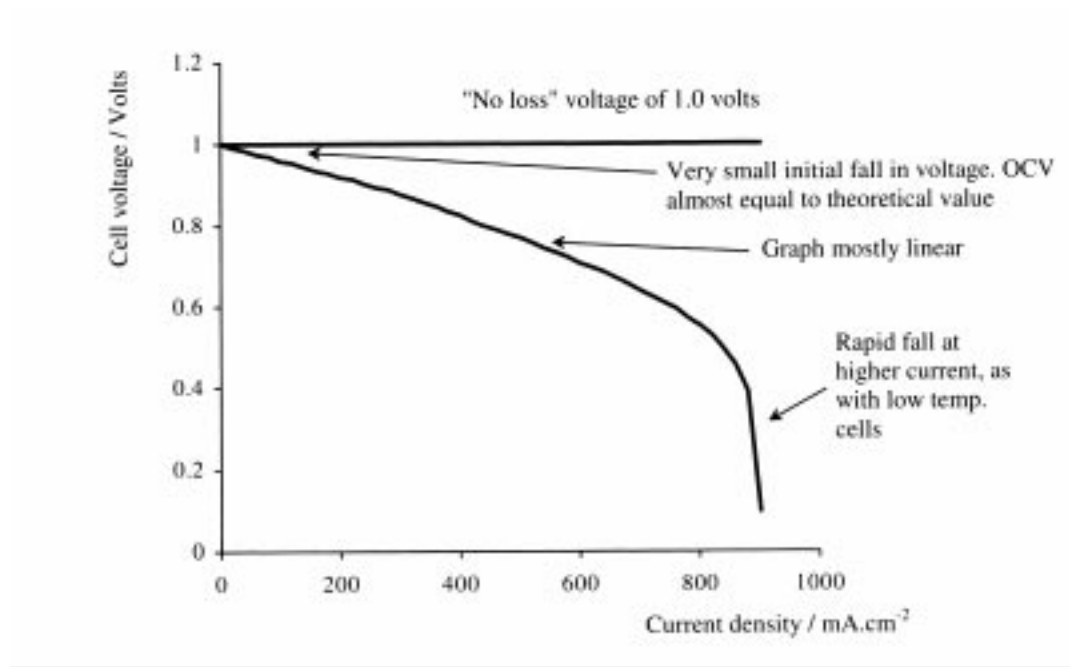


Figure 4.2: High Temperature Fuel Cell Losses

This voltage is not the operational voltage of fuel cell, as Fig. 4.1 and Fig. 4.2 have shown us. Our first task is to show why the initial theoretical voltages are different. By applying Eq. (4.1) alone we can see that the EMF of the fuel cell is directly dependant on the desired operational temperature, this is the case because we have seen in the last chapter that V is directly dependant on temperature [13]. Fig. 4.3 shows the application of Eq. (4.1) to temperatures in the 200 K to 1200 K range. Fig. 4.3 shows us why the low temperature fuel cells have a theoretical EMF of 1.2V and why the high temperature fuel cells have a theoretical EMF of 1.0V .

4.2.2 Description of Operational Losses

The losses that were evident in Fig. 4.1 and Fig. 4.2 can be broken up into four different types of losses. These are activation losses, fuel crossover/internal current losses, ohmic losses, and mass transport/concentration losses. These losses each have a different effect on the theoretical voltage of the fuel cell. The activation loss occurs because the chemical process initially has not begun, thus activation energy is necessary insure that the reaction tends toward the formation of water and electricity, as opposed to the reverse. This loss only occurs at low current densities in low temper-

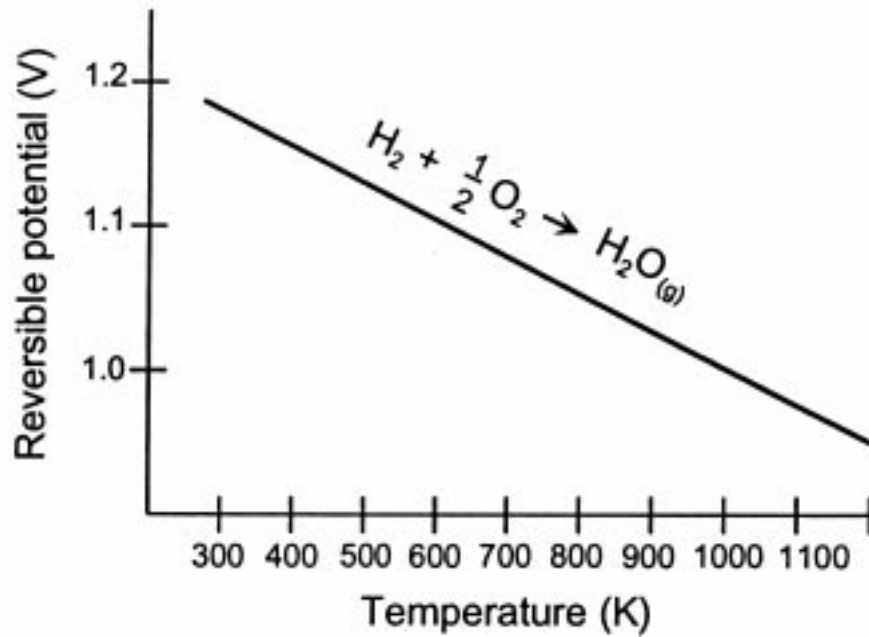


Figure 4.3: Temperature Dependence

ature fuel cells. The second source of loss is the fuel crossover/internal current loss. This loss is associated with the losses that occur through the electrolyte. It can occur in two ways, either fuel leaking through the electrode or electrons leaking through the electrode. Fuel leakage causes most of the problems in this category, and just like the activation energy loss this loss only has a significant effect at low temperatures. The most common source of loss in any electrical device is also present in the fuel cell, and those are Ohmic losses. This type of loss occurs because of the resistance to the flow of electrons in the interconnect, the anode and the cathode. This loss, like all Ohmic losses, is directly proportional to the current. It appears as a major source of loss in both the low and high temperature fuel cells. The final type of loss is the mass transport/concentration loss. This loss occurs in both low and high temperature fuel cells, but is only prevalent at high current densities. It is the result of the effect of losing a high concentration of either fuel or oxygen at the anode and cathode, respectively. It essentially occurs because the fuel cell is using fuel or oxygen faster than it can be supplied. All of these losses contribute in their own way to form the operational voltages that can be seen in fuel cells today.

4.3 Activation Losses

Activation losses are those losses associated with the initial dramatic voltage losses in low temperature fuel cells. These losses are basically representative of a loss of overall voltage at the expense of forcing the reaction to completion, which is forcing the hydrogen to split into electrons and protons, and for the protons to travel through the electrolyte, and then combine with the oxygen and returning electrons. This loss is often termed over potential, and is essentially the voltage difference between the two terminals. Through experimentation Tafel was able to mathematically describe these losses.

4.3.1 Tafel Equation

Through experimentation Tafel produced figures that showed direct correlation between the current density and the output voltage, at lower currents. The plot has been displayed in natural logarithm form to simplify the analysis. The corresponding equation for the experiment is below, one being a slow reaction the other a fast reaction.

$$V = A \ln \left(\frac{i}{i_o} \right) \quad (4.2)$$

The constant A is higher for those reactions that are slower, and the constant i_o is larger for faster reactions. The value of i_o called the exchange current and becomes important later when we discuss the exchange current losses. i_o is the value on the Tafel plot when the current begins to move away from zero. The following graph illustrates the effects of the constants in the Tafel equation.

For determining the values of A in the experimental Tafel equation there has been work done to show what a theoretical value would be. The following equation has been simplified to apply specifically to a hydrogen fuel cell. [9].

$$A = \frac{RT}{2\alpha F} \quad (4.3)$$

In this equation R is the ideal gas constant, T is the temperature in Kelvin or Rankie, and F is the Faradays constant. The value α is known as the charge transfer coefficient, and is unitless. This value describes the proportion of the electrical energy applied that is harnessed in changing the rate of an electrochemical reaction. [9] It is this value that differs from one material to another. Thus the overall value of A is simply a function of the material properties. For typically used materials the value is in a very narrow range; it is always about $\alpha = .5$ for the electrode, and it ranges from about $\alpha = .1$ to $\alpha = .5$ for the cathode. These minor variations make

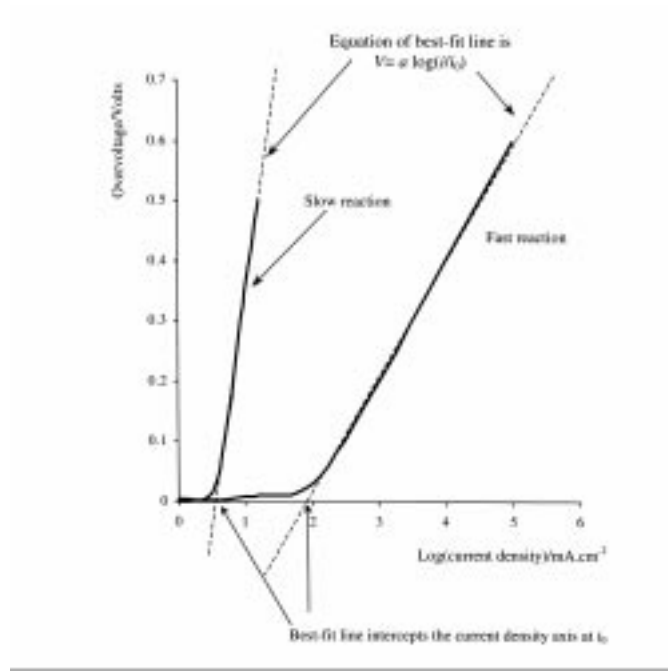


Figure 4.4: Tafel Plot

experimenting with different material to dramatically change the voltage predicted by the Tafel equation not a very productive endeavor. At this point it is useful to look back on Eq. (4.2), as we can see from the form of the equation the only constant that we can change is i_o . The exchange current density constant varies over a range of four orders of magnitude, and thus has a dramatic effect on the performance of fuel cells at low current densities. To gain a more quantifiable understanding of how this value effects the voltage, the Tafel equation was plotted for several of these values of i_o , and it was seen that if a low end value of i_o ($.001 \frac{mA}{cm^2}$) is used then the current steadies around .6 V, and a high end value of i_o ($100 \frac{mA}{cm^2}$) is used then the steady voltage is 1.1 V. This dramatic effect illustrates why it is vital to design fuel cells with high exchange current densities.

4.3.2 Maximizing the Tafel Equation

The goal of fuel cell design, as it is in all design processes is to produce the most efficient product. In this specific case that means that we have to keep losses at a minimum. In order to minimize the loss of voltage due to activation losses there are several things that can be done. First, we can increase the operational temperature.

As Fig. 4.1 and Fig. 4.2 shows the activation loss at high temperatures is minimal. This is due to the fact that the value of i_o increases almost two orders of magnitude over the span of temperatures typically used. Secondly, we can increase catalytic presence. This can be accomplished in three effective ways. First we can use rougher catalysts, this allows for more area of contact and thus allows the reaction to proceed faster. Secondly to increase catalytic effects you can increase the operational pressure. This is true since the higher the pressure at the cathode the quicker the reaction will be “forced” to take place, also we have seen in Chapter 3 that the increase of pressure is helpful to increasing the voltage of the cell. The final way to increase the catalytic effect is to use a more effective material. The following table illustrates the range of i_o values for a variety of materials at STP.

Metal	$i_o \left(\frac{mA}{cm^2} \right)$
Pb	2.5×10^{-13}
Zn	3.0×10^{-11}
Ag	4.0×10^{-7}
Ni	6.0×10^{-6}
Pt	5.0×10^{-4}
Pd	4.0×10^{-3}

Table 4.1: Common i_o values for selected Metals

The use of a more valuable catalyst can be very rewarding since the value of i_o that is associated with commonly used metals ranges from 10^{-13} up to 10^{-3} . Today, mainly in the interest of cost, Nickel or Platinum is used. As mentioned above, these values will all increase as the temperature and pressure are increased.

4.4 Fuel Crossover/Internal Current Losses

The next portion of the graph that needs to be investigated is the cause of low temperature fuel cells having a lower initial voltage, that is their OCV is .3 V less than what theory predicts. This initial loss of voltage is due to fuel crossover and internal currents. These two sources of voltage loss are grouped together because despite being different modes of loss they contribute to the loss in the same amount and they both occur due to the inability to produce a perfect electrode. The electrode, as described in Chapter 2, is the region of a fuel cell that separates the anode from the cathode, and provides a means for the proton transfer. The electrode is often made of different materials depending on the type of fuel cell, and is either a solid or a liquid. The electrode is porous, necessary to allow proton transfer, and is also

slightly conductive, as a result it is possible for un-reacted fuel and electrons to crossover to the cathode. Since in both of these processes two electrons are wasted, prevented from traveling externally, the losses are similar in source and the same in result. In order to model this phenomenon the Tafel equation that was used earlier, Eq. (4.2), can be modified. This modification will allow for the addition of the term $i_n \frac{mA}{cm^2}$.

$$V = A \ln \left(\frac{i + i_n}{i_o} \right) \quad (4.4)$$

This new form of the Tafel equation will now account for the initial loss of voltage in low temperature fuel cells. It is not prevalent in high temperature fuel cells because the small value of i_n does not significantly change the ratio in the natural logarithm, i_n is usually less than 10.

4.5 Ohmic Losses

Ohmic losses are prevalent in every electronic device, and fuel cells are not an exception to this rule. These losses simply occur due to the resistance to electron flow in the bipolar plates, described in Chapter 2. They are of the standard Ohmic form, but usually written in terms of current density and area resistance. This allows for the ease of use in evaluating performance of the cell, since most cells are rated in terms of the current density.

$$V = ir \quad (4.5)$$

where i is the current density and r is the area specific resistance. Thus to reduce the value of the Ohmic resistance it is necessary to use electrodes with extremely high conductivities, or reducing the distance that the electrons must travel; resistance is proportional to distance. Another way to reduce the resistance is to use well-designed bipolar plates, which have high conductivities and short lengths. The final way to reduce resistance associated with Ohmic losses is to create a thin electrode, thus giving the protons a shorter distance to travel before they can combine with the oxygen and electrons.

4.6 Mass Transport/Concentration Losses

The losses that occur due to mass transport/concentration problems are those directly related to the pressure issues that were discussed in Chapter 3. If the hydrogen is being used at a very vigorous rate at the anode then the partial pressure of the

hydrogen drops, thus slowing the reaction rate. This is also the same case that occurs at the cathode with oxygen. To mathematically model this situation we must modify our voltage equation that we developed in Chapter 2. This relationship is the change in voltage relationship for the hydrogen.

$$\Delta V = \frac{RT}{2F} \ln \left(\frac{P_2}{P_1} \right) \quad (4.6)$$

To adapt this equation we assume a limiting current density i_l at which the fuel is used up at a rate equal to its maximum supply speed [9]. This will act as a current ceiling since there will be no more fuel to advance the density, that is to say the pressure of excess hydrogen will be zero. If we define P_l as this pressure, then assume a linear current density that runs from the current at no pressure down to the limiting pressure at maximum current then the following relationship can be applied.

$$P_2 = P_l \left(\frac{i_l - i}{i_l} \right) \quad (4.7)$$

To fully develop the model this equation must be plugged into the voltage relationship developed earlier. This produces the final relationship:

$$\Delta V = \frac{RT}{2F} \ln \left(1 - \frac{i}{i_l} \right) \quad (4.8)$$

Eq. (4.8) shows us that most of the loss occurs near the limiting value of i_l , thus following with our figures in the beginning of the chapter. This type of loss is also considered a Nernstian loss since it uses the Nernst equation to determine the change in voltage.

4.7 Conclusion

4.7.1 Combining the Losses

If all the losses that we have looked at: activation, fuel crossover, mass transport, and ohmic losses are combined then the actual operational graph of a fuel cell is produced. This graph Fig.4.5 below is the curve that is used to determine if the specific fuel cell is operating at high standards. The equation for this line is given in Eq.(4.9).

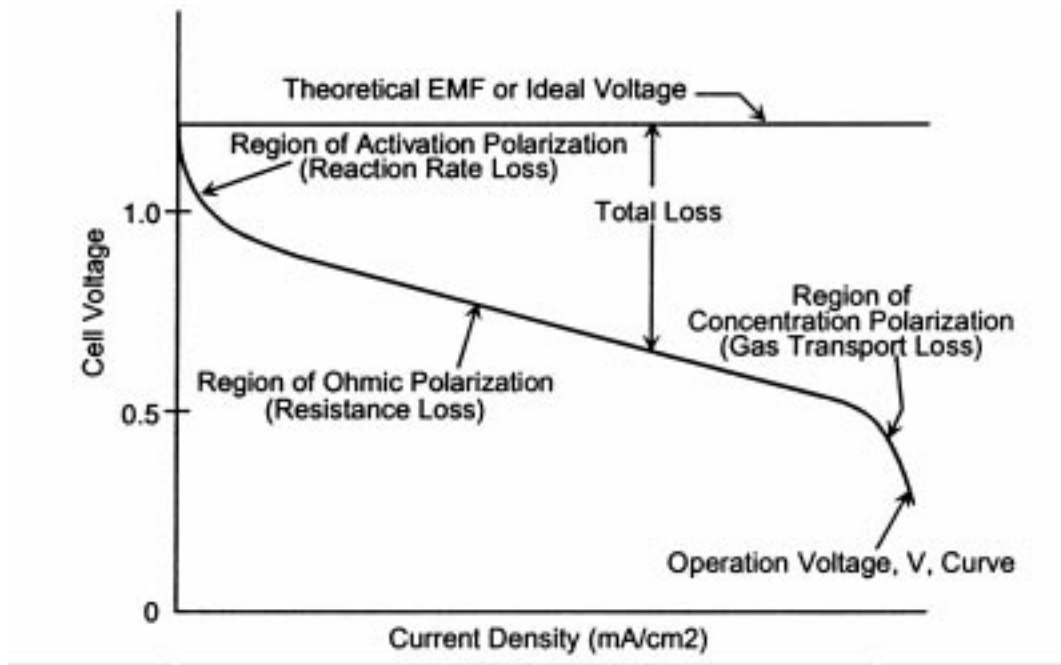


Figure 4.5: Operational Fuel Cell Plot for Voltage vs. Current Density

$$\Delta V = E - (i - i_n)r - A \ln \left(\frac{i + i_n}{i_o} \right) + B \ln \left(1 - \frac{i + i_n}{i_l} \right) \quad (4.9)$$

Chapter 5

Alkaline Fuel Cells

Alkaline fuel cells differ from other types of fuel cells in the chemical reaction and the operating temperature. The basic schematic of an alkaline fuel cell is given in Fig. 5.1.

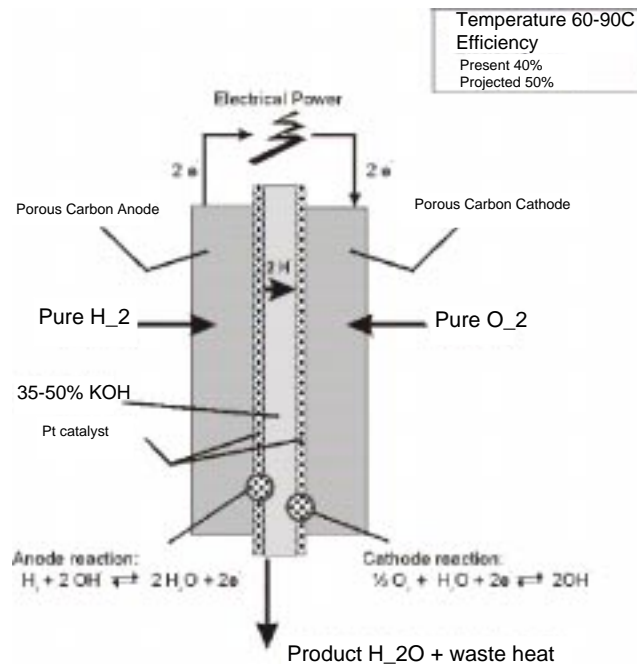
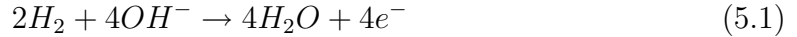


Figure 5.1: Basic Alkaline Fuel Cell

The chemical reaction that occurs at the anode is:



The reaction at the cathode occurs when the electrons pass around an external circuit and react to form hydroxide ions, OH^- , as shown:



It was not until the 1940's that F.T. Bacon at Cambridge, England proved alkaline fuel cells as a viable source of power. Alkaline fuel cells were used in the Apollo space shuttle which took the first men to the moon. Due to the success of the alkaline fuel cell in the space shuttle Bacon was able to perform much research toward alkaline fuel cells. They were tested in many different applications including agricultural tractors, power cars, and provided power to offshore navigation equipment and boats.[9] Alkaline fuel cells encountered many problems including cost, reliability, ease of use, durability, and safety which were not easily solved. Attempts at solving these problems proved to be uneconomical given the other sources of energy at the time. Proton exchange membrane fuel cells became very successful and therefore alkaline fuel cells were given much less development resources. The space program remained an important researcher for alkaline fuel cells and since has improved alkaline fuel cells.

Alkaline fuel cells have some major advantages over other types of fuel cells. The first is that the activation overvoltage at the cathode is usually less than with an acid electrolyte fuel cell. The second advantage is that the electrodes do not have to be made of precious metals.

5.1 Types of Alkaline Electrolyte Fuel Cells

Alkaline fuel cells are categorized depending on their pressure, temperature and electrode structure which widely varies between the different designs. The one major commonality between all alkaline fuel cells is the use of potassium hydroxide solution as the electrolyte.

5.1.1 Mobile Electrolyte

The mobile electrolyte fuel cell uses pure hydrogen, H_2 , as the fuel at the anode and air for the reaction at the cathode. The electrolyte is pumped around an external circuit. The hydrogen must be circulated to extract the water produced by means of a condenser. This is due to the fact that the hydrogen evaporates the water product. One of the major problems that the mobile electrolyte fuel cell faces is the chemical

reaction between the potassium hydroxide electrolyte, KOH , and carbon dioxide, CO_2 , that is present in the supplied air. The problem is shown in the following reaction:



We can see that the potassium hydroxide is slowly converted to potassium carbonate in the presence of carbon dioxide. This is unfavorable because the efficiency and performance of the fuel cell depends on keeping the potassium hydroxide in its pure form. To avoid this problem, a carbon dioxide scrubber is used to remove as much carbon dioxide as possible from the supplied air. This type of fuel cell was used in the Apollo space shuttle. The carbon dioxide problem is the reason the astronauts in the movie Apollo 13 had to build their own carbon dioxide scrubbers to keep power supplied to the space shuttle.

The major advantages of the mobile electrolyte fuel cell are [13]:

- The fuel cell can be easily cooled by using the circulated hydrogen.
- The circulated potassium hydroxide helps to avoid the produced water from becoming saturated in the potassium hydroxide and therefore solidifying.
- The setup makes it very easy to completely replace all the electrolyte if the need arises such as in the case that the electrolyte reacts with carbon dioxide as in Eq. (5.3) and becomes unusable.

5.1.2 Static Electrolyte Alkaline Fuel Cells

Static electrolyte fuel cells differs from mobile electrolyte fuel cells in that the electrolyte is held in a matrix material, and therefore does not circulate as in the mobile fuel cell. Static fuel cells usually use pure oxygen as the reactant for the cathode side, but does not have to be in pure form. The hydrogen is circulated to remove the gaseous form of water product. An individual cooling system is needed to keep the fuel cell within an operational temperature range.

5.1.3 Dissolved Fuel Alkaline Fuel Cells

The dissolved fuel alkaline fuel cell is the simplest alkaline fuel cell to manufacture and examples how simple such a fuel cell can be. Dissolved fuel alkaline fuel cells do not work well for large power generation applications. Potassium hydroxide is used as the electrolyte along with a fuel such as hydrazine, or ammonia combined with it. This type of fuel cell has very high fuel crossover problems but it is not of great importance since the cathode catalyst is not platinum.

The optimum fuel to be used by this type of fuel cell is hydrazine, H_2NNH_2 , because it dissociates into hydrogen and nitrogen on the surface of a fuel cell electrode. The resulting hydrogen can then be used as the fuel. It is unfavorable to use this fuel because hydrazine is toxic, a carcinogen, and explosive. Therefore, even though fuel cells using this fuel might be simple, they are rarely widely used.

As a result of the problems which arise when using hydrazine, an alternative fuel such as methanol can in theory be used. The methanol reaction at the anode is:



but as we can see, the produced CO_2 will react with the KOH as shown in Eq. (5.3) thus producing carbonate which is unfavorable. Since the carbon dioxide cannot be easily removed from the system, the use of methanol is impractical. Even though acid electrolyte fuel cells could be used with the dissolved fuel principle, but it is very difficult to “make an active catalyst in a low temperature acid electrolyte fuel cell that does not use precious metals, and that will not therefore oxidize the fuel.” [9]

5.2 Electrodes for Alkaline Electrolyte Fuel Cells

Alkaline electrode fuel cells operate at a wide range of temperatures and pressures and their application is very limited. As a result, there are different types of electrodes used. Some of the various types of electrodes are explained below.

5.2.1 Sintered Nickel Powder

Sintered nickel powder was used by F.T. Bacon in his first fuel cell because of the low cost and simplicity of the material. The powder form of the nickel makes it much more porous and therefore more advantageous for fuel cells since the porosity increases the surface area for the chemical reactions to take place on. The sintering is used to make the powder a rigid structure. Two different sizes of nickel powder are used to give the optimum porosity for the liquid and gas fuel. The liquid is better with a smaller pore size, and larger for the gas fuel. The Apollo space shuttle used this type of electrode structure. [9]

5.2.2 Raney Metals

Raney metals are a good solution to achieving the activity and porosity needed in an electrode. A Raney metal is formed through mixing an active metal needed for the electrode and an inactive metal such as aluminum.[9] The inactive metal is then removed from the mixture by dissolving the metal using a strong alkali. The remaining

structure is a highly porous structure made entirely of active metal. An advantage of this process is that the pore size can be easily changed for the desired application by simply altering the mixture ratio of active to inactive metal. Raney metals are often used for the anode, or negative side of the fuel cell, and silver for the cathode, or positive side of the fuel cell.[9] Raney metals were also incorporated into the fuel cell technology used on submarines by Siemens in the early 1990s. [9]

5.2.3 Rolled Electrodes

Carbon supported catalysts are commonly used in the current production of electrodes. They are also mixed with polytetrafluoroethylene (PTFE). This combination is then rolled onto a sheet of nickel. The purpose of the PTFE is to act both as a binder and control porosity in the mixture. Due to the strength to weight ratio and the conductivity, carbon fiber is often used to increase the strength, conductivity and roughness of the mixture. Rolled electrode manufacturing can be performed on an altered paper machine which makes it easily manufactured at a relatively low cost. [9] The use of non-platinum electrodes greatly reduces the cost of producing the electrodes. The cost for such electrodes is approximately $\$0.01/cm^2$ or about $\$10/ft^2$. [9]

There are problems associated with rolled electrodes. The electrode has a layer of PTFE which is nonconductive and therefore a bipolar plate is unusable for connecting multiple cells. The problem of carbon dioxide, explained by Eq.(5.3), is present when carbon supported catalysts are used in the electrode. The carbon dioxide can be removed which increases the lifetime of the fuel cell, but this causes much lower current densities which are unfavorable. Guzlow (1996) used an anode based on granules of Raney nickel mixed with PTFE which does not use carbon supported catalysts to try and solve this problem.[9] Apparently this type of electrode does not react to the CO_2 making it highly favorable for use in this type of application.

5.3 Operating Pressure and Temperature

Alkaline electrolyte fuel cells generally operate at pressure and temperature much higher than the environment it operates in. As we can see from Chapter 3, the open circuit voltage of a fuel cell depends on the temperature and pressure and increases with increasing pressure and temperature. The actual increase in voltage is much higher given that the pressure increase increases the exchange current density which reduces the activation overvoltage on the cathode. [9]

Other problems arise with high pressure storage systems and cryogenic storage systems. There is an increased cost to manufacture systems that ensure no leakage

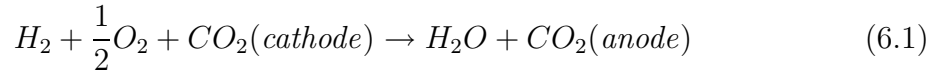
in the high pressure systems. It is essential in this type of storage device to ensure no leaks because of the high flammability of pure hydrogen and oxygen. One solution is to encase the fuel cell inside a pressure vessel with an inert gas of higher pressure than that of the fuel cell. This ensures that any leaks do not escape the fuel cell, but instead the inert gas, such as nitrogen as used by Siemens, flows into the fuel cell ensuring no leakage of combustible fuels.[13]

Chapter 6

Molten Carbonate Fuel Cell

The defining characteristic of a molten carbonate fuel cell (MCFC) is the material used for the electrolyte. The material is a molten mixture of alkali metal carbonates. The electrolyte is usually a binary mixture of lithium and potassium, or lithium and sodium carbonates which is held in a ceramic matrix of $LiAlO_2$. [9] A highly conductive molten salt is formed by the carbonates at very high temperatures (approximately 600-700 °C). [9]

A general schematic of a molten carbonate fuel cell is shown in Fig. 6.1. Note that unlike the alkaline fuel cells, carbon dioxide must be supplied to the cathode instead of being extracted from the supply. The carbon dioxide and oxygen is essential to react and form the carbonate ions by which the electrons are carried between the cathode and anode. Note that there are two moles of electrons and one mole of CO_2 transferred from the cathode to the anode. This is given by Eq.(6.1):



As described in Ch.2 we can determine the Nernst reversible potential for a molten carbonate fuel cell as given below:

$$E = E^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right) + \frac{RT}{2F} \ln \left(\frac{P_{CO_{2c}}}{P_{CO_{2a}}} \right) \quad (6.2)$$

where a and c correspond to the anode and cathode gas supplies respectively.

The CO_2 produced at the anode is commonly recycled and used by the cathode. This allows the reactant air to be preheated while burning unused fuel and the waste heat can be used for alternate purposes as necessary. This configuration also allows the CO_2 to be supplied externally from a pure CO_2 source. Another advantage with

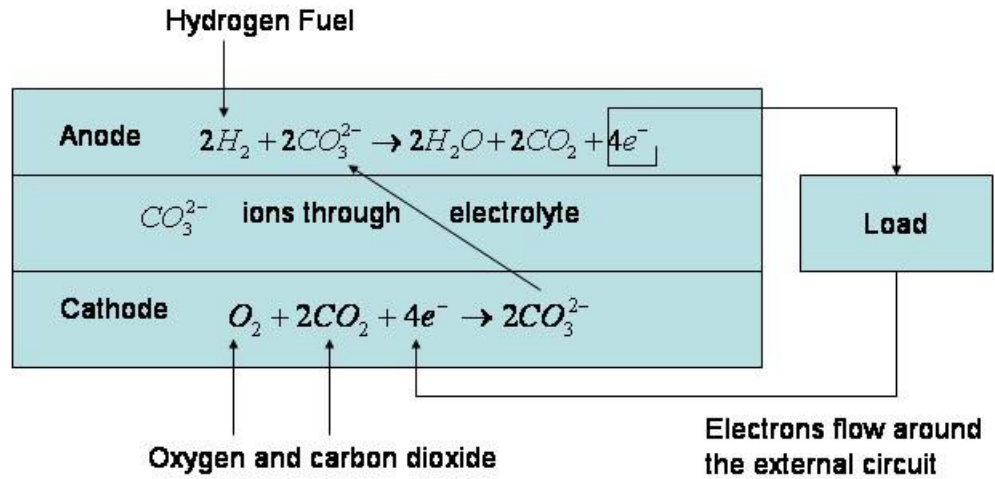


Figure 6.1: General schematic of reactions within a molten carbonate fuel cell

molten carbonate fuel cells using this setup is that they do not require noble metals for the electrodes.

An alternative to supplying hydrogen to the anode, is supplying carbon monoxide as the fuel to the anode. The difference is that twice the amount of carbon dioxide is produced at the anode instead of water, and the same amount of electrons are produced. The reversible open circuit voltage can be determined and is identical to that given in Chapter 3:

$$E = \frac{-\Delta\bar{g}_f}{2F} \quad (6.3)$$

Some values for the gibbs free energy and open circuit voltage are given in Table 6.1.

Molten carbonate fuel cells operate at relatively high temperatures which allow them to attain high efficiencies. Their high operating temperature also allows them to utilize different fuels as shown above with the use of carbon monoxide.

Fuel	$\Delta\bar{g}_f/KJ.mol^{-1}$	E/Volts
H_2	-197	1.02
CO	-201	1.04

Table 6.1: Values of $\Delta\bar{g}_f$ and E for hydrogen and carbon monoxide fuel cells at $650^\circ C$

6.1 Molton Carbonate Fuel Cell Components

6.1.1 Electrolytes

Current molten electrolyte fuel cells contain approximately 60 wt% carbonate in a matrix of 40 wt% $LiOAlO_2$. The $LiOAlO_2$ is made of fibers approximately $< 1\mu m$ in diameter. The matrix is produced using tape casting similar to those used in the ceramics and electronics industry. The ceramic materials are put into a "solvent" during the manufacturing process. A thin film is formed on a smooth surface by use of an adjustable blade device. The material is then heated and organic binding agents are burned out. The thin sheets are then put on top of each other to form a stack. The operating voltage is largely related to the ohmic resistance of the electrolyte. The most significance factor of ohmic losses is the thickness of the electrolyte described by [9]:

$$\Delta V = 0.533t \quad (6.4)$$

where t is the thickness of the electrolyte in cm . Currently using tape casting, the electrolyte thickness can be reduced to approximately $0.25 - 0.5 mm$.

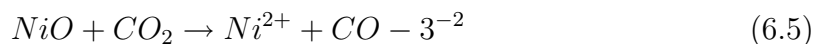
6.1.2 Anodes

Molton carbonate fuel cells are made of porous sintered Ni-Cr/Ni-Al alloy. The anodes can be made to a thickness of 0.4-0.8 mm. The anodes are manufactured using hot pressing fine powder or tape casting as used for the electrolytes. Chromium is commonly added to reduce the sintering of the nickel, but causes problems such as increased pore size, loss of surface area and mechanical deformation under compressive load in the stack. [9] These problems can be reduced by adding aluminum to the anode.

The reactions that take place at the face of the anode are relatively fast at high temperatures, therefore a large surface area is not needed. This reduces the amount of porosity needed in the structure. This allows partial flooding of the anode with molten carbonate without problems. Tape casting allows the anodes to be manufactured with a various porosity throughout the anode which can be favorable given that larger pores near the fuel gas channel is optimal.

6.1.3 Cathode

The cathode of a molten carbonate fuel cell is made of nickel oxide. The problem with nickel oxide is the solubility in molten carbonates. Nickel ions diffuse into the electrolyte towards the anode. Metallic nickel will then precipitate out in the electrolyte. This precipitation will cause internal shortages within the fuel cell which cause electrical problems. The formation of nickel ions is described by the equation:



which can be reduced using a more basic carbonate in the electrolyte. Nickel dissolution can be reduced by (a) using a basic carbonate, (b) reducing the pressure in the cathode and operating at atmospheric pressure, and (c) increasing the thickness of the electrolyte to increase the amount of time and distance it takes for Ni^{2+} to reach the anode.

6.1.4 Manifolding

Molten carbonate fuel cells need manifolds to supply the gases for operation. This is done by the use of *external* or *internal manifolds*. With external manifolds the bipolar plates are approximately the same size as the electrodes. External manifolds were described in the explanation of fuel cells in Chapter 2. External fuel cells are a very simple design, they allow low pressure drop in the manifold and efficient flow through the manifold. A drawback is the temperature gradients caused by the flow of gases perpendicular to each other. External manifolds can also have leakage problems.

Internal manifolds allow gas distribution internally or within the stacks themselves, by penetrating the separating plate. Internal manifolds allow much more diversity in the direction of flow of gasses to minimize temperature gradients. They also allow a high degree of variation in the stack design. The electrolyte matrix is used as the sealant in the internal manifold.

6.2 MCFC research and systems

As of the printing of Laraminie and Dicks book on fuel cells, there were two corporations within the U.S. conducting research toward the commercialisation of molten carbonate fuel cells.[9] These are Fuel Cell Energy (formerly Energy Research Corporation) and M-C Power Corporation. Fuel Cell energy has demonstrated a 2 MW molten carbonate fuel cell, and MC Power has demonstrated a 250 kW fuel cell. Japan currently has a 1 MW MCFC plant running. MCFCs should be close to becoming commercialized within the next few years.[9]

Chapter 7

Polymer Electrolyte Fuel Cell (PEMFC)

7.1 Introduction

Polymer electrolyte fuel cells have the ability to operate at very low temperatures; this is the main attraction of the PEM. Since they have the ability to deliver such high power densities at this temperature they can be made smaller which reduces overall weight, cost to produce and specific volume. Since the PEM has an immobilized electrolyte membrane there is simplification in the production process that in turn reduces corrosion, this provides for longer stack life [13]. This immobilized proton membrane is really just a solid-state cation transfer medium. Various groups will call these types of cells SPFC, for solid polymer fuel cells, this is usually in government setting since the federal government will more generously fund solid state energy. The PEM, like all fuel cells, consists of three basic parts; the anode, the cathode, and the membrane. These three areas are often manufactured from separate “sheets”, and the PEM is no exception. The anode and electrode are often formed together, thus making a membrane electrode assembly (MEA). The PEM has been in use for some time by the government, making its debut on the Gemini, its life was only 500 hours. After NASA’s decision to use alkaline fuel cells on subsequent missions the popularity of PEM fell dramatically, until recent advances made them more economical to develop and research. With the development of new membranes, such as Nafion, and the reduction in Pt use (from $28 \frac{mg}{cm^2}$ in 1967 down to $.2 \frac{mg}{cm^2}$ today). PEMs are being actively pursued for use in automobiles, busses, portable applications, and even for some CHP applications. Today industry has great hope for the PEM, some even sighting that it has exceeded all other electrical energy generating technologies in the breadth of scope and their possible applications.[9] The PEM, is potentially the most

important fuel cell being researched today.

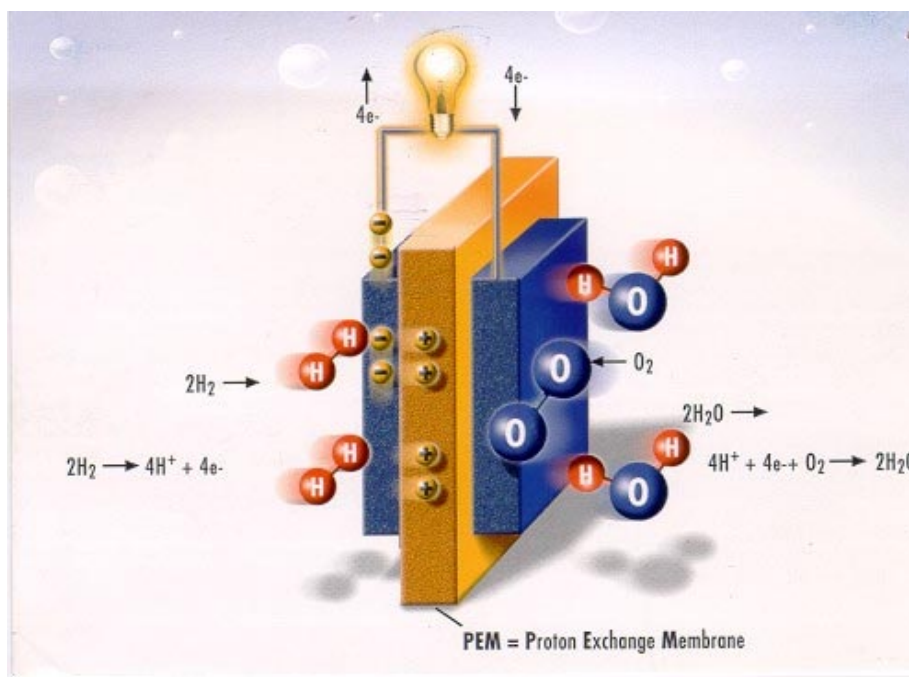


Figure 7.1: PEM: A General Cell

7.2 The Polymer Membrane

The PEM is named for the solid-state exchange membrane that separates its electrodes. William Grubbs discovered in 1959 that without the presence of strong acids in his membrane he was still able to transfer cations, protons, to the cathode.[13] This discovery was capitalized on by NASA, and is still being used today. This membrane is just a hydrated solid that promotes the conduction of protons. Although many different types of membranes are used, by far that most common is Nafion, produced by DuPont. Other types of membranes being researched are; polymer-zeolite nanocomposite proton-exchange-membrane, sulfonated polyphosphazene-based membranes, and phosphoric acid-doped poly(bisbenzoxazole) high temperature ion-conducting membrane. Although the Nafion membrane is so commonly used it is considered an industry standard, and all new membranes are compared to it. The Nafion layer is essentially a carbon chain, which has a Fluorine atom layer attached to it. This is considered Teflon. A branch is formed off of this basic chain (also made of carbon

atoms surrounded by Fluorine), the frequency of these side chains are reflected in the types of Nafion. The side chains increase the hydrophilic effect of the material. This property of the Nafion allows for up to 50% increase in dry weight. All of these properties result in five important properties of the material [9]:

- they are highly chemically resistant
- they are mechanically strong (possible to machine them as small as $50\mu m$)
- they are acidic
- they are very absorptive to water
- they are good proton (H^+) conductors if well hydrated

The membrane allows for the transfer of protons and thus permits the general fuel cell process, which is similar to the PAFC. Hydrogen at the anode separates the electron and proton, freeing them to travel throughout the fuel cell. The electron travels externally, while the proton travels through the conductive membrane to the cathode. This is accomplished by being solvated in water molecules, thus the need for a hydrated membrane. The electron and proton then meet at the cathode where water is formed, in the presence of oxygen. Since high temperatures are not necessary to hydrate the membrane the PEM can be run at very low temperatures, typically at $80^\circ C$ or lower.

7.3 Water Management

The main concern that has to be considered in the polymer electrolyte membrane is the management of water. This is an issue because liquid is produced as a final product, as opposed to steam. Since this water product is formed it is important not to flood the electrolytes. Flooding of the electrodes causes a decrease in surface area in which the separation of hydrogen or the formation of water takes place. The water cannot be simply removed, since as mentioned above the membrane needs to be hydrated; thus a balance must be achieved. The water that is formed at the cathode must be regulated by removal or retention techniques. Since the electrode is very thin ($50\mu m$) is possible for the water to leak back to the anode, which would be the ideal situation if the exact amount were to migrate. This is ideal since the electrode needs to remain hydrated to promote the high levels of proton transfer, the water transfers the protons through the membrane. Several complications arise in this process. The first is that the water naturally moves toward the cathode, about 1 to 2.5 molecules per proton [9]. This "electro-osmotic drag" is problematic at high

Electrolyzer Cell Mode

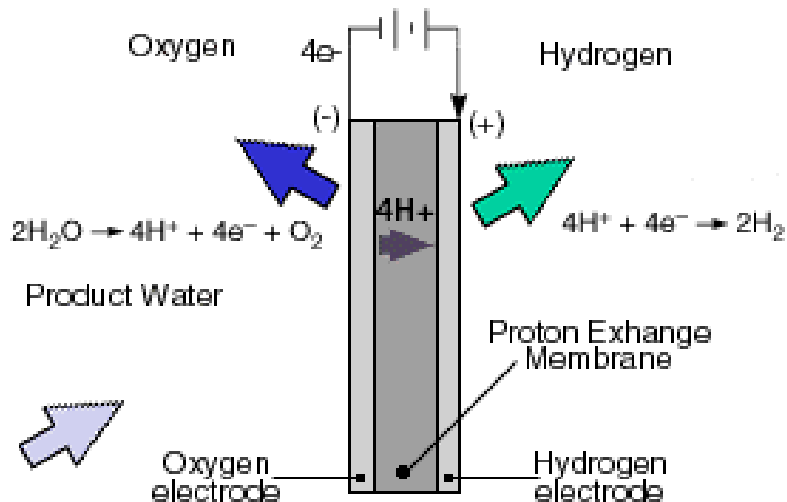


Figure 7.2: Schematic of the Cell

current densities because all the water can be removed from the anode, thus causing an abrupt loss in fuel pressure since no water will be present to transfer new protons (this is a form of a mass transportation loss). A further problem in water management is the susceptibility to have the air dry the water out at high temperatures. Studies have shown that at temperatures over 60°C the air dries out the cathode. To solve this problem it is necessary to add water to the system to keep everything hydrated, the trick is not to over hydrate the cell. To date all types of water management problems that have major impact on cell performance have been solved. Although these problems have been solved it is still quite necessary to understand these issues since design of a cell is critically based on water management.

7.3.1 Air Flow's Contribution to Evaporation

Air is supplied to the cell to provide oxygen to the cathode. The presence of the air also provides a vehicle for which excess water can be removed from the system, or in a detrimental case dry the cell out. In order not to remove too much water from the cathode, thus drying the membrane and the anode out, it is necessary to have the correct airflow. The following equation, Eq.(7.1) is derived from the definition of

power, and O_2 usage in the cell [9].

$$Air\ flow\ Rate_{cathode} = 3.57 \times 10^{-7} \times \lambda \times \frac{P_e}{V_c} \quad (7.1)$$

The λ represents the stoichimetric ratio, in the case of the PEM $\lambda = 2$. The P_e is the power of the cell and the V_c represents the voltage of the cell. Since problems arise due to the fact that the drying effect is highly non-linear with respect to the room temperature we must define a few special terms. [9] These terms allow us to qualitatively describe the necessary water conditions in the cell.

- Humidity Ratio, $\varpi = \frac{m_w}{m_a}$

Where m_w is the mass of water percent in the sample of the mixture, and m_a is the mass of the dry air.

- Relative Humidity, $\theta = \frac{P_W}{P_{sat}}$

P_W is the partial pressure of the water, and P_{sat} is the saturated vapor pressure. These values are typically in the range of 30% to 70%.

By using the humidity ratio, relative humidity and the exit air flow rate equation we arrive at the pressure relationship for the PEM.[9] Eq.(7.2) simply establishes that the vapor pressure at the exit is a function of the air properties and the operating pressure of the cell.

$$P_W = \frac{.421}{\lambda + 0.188} P_t \quad (7.2)$$

Where P_W is the partial pressure of water in the air, and P_t is the operating pressure. In order to complete the process we must add the fact that the temperature plays a very important role. The result of adding the temperature into the equation results in a decaying exponential. This graph is maximized in the region where the cathode will not be too dry or wet, typically $60^\circ C$, see Fig. 7.3.

7.4 Effects of Pressure

The advantages of operating PEMs at elevated pressures are often debated. To pressurize the system there are certain costs; monetary, size, weight, etc. There are also benefits, the major benefit is to supercharge the system, which is to get a higher power rating out of a smaller device. The question of pressurization is only used in larger PEMs ($10kw \geq$). A simple example of a pressurized fuel cell would be if a pressurized hydrogen container feeds it. In this example a motor would be powered

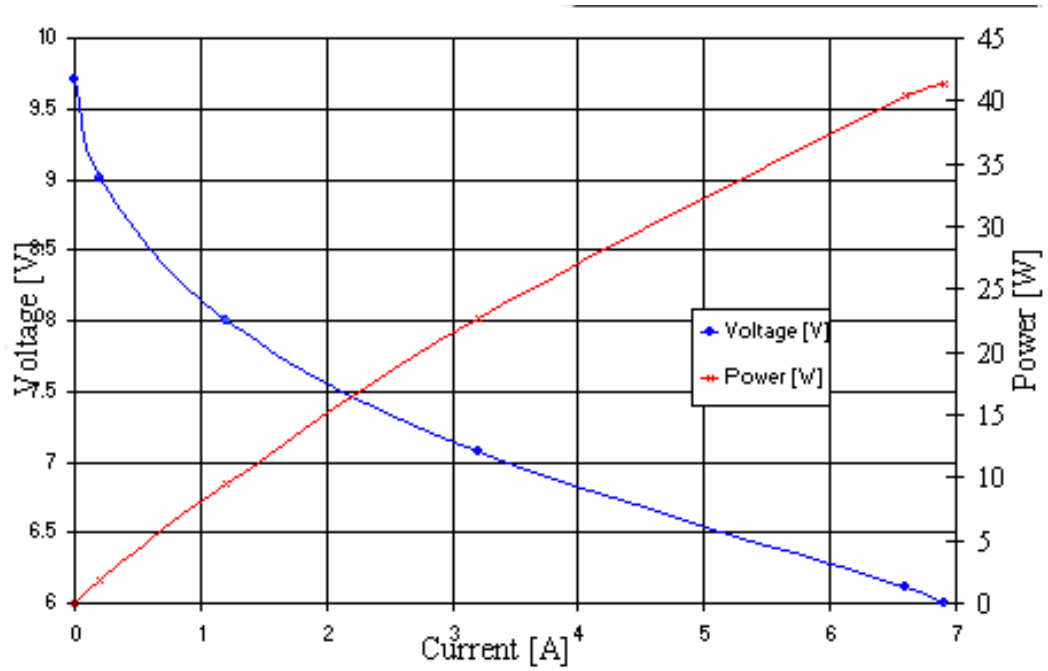


Figure 7.3: Temperature Dependence of the Cell

by the fuel cell to compress the intake air, which would be necessary to supply an adequate amount of O_2 and satisfy water concerns. An evaluation of this system can be made and then compared to the un-pressurized system. Does the effect of increasing the power, via the rate of the process, outweigh the cost of compressing the gas? To gain a more factual understanding of the answer to this question we must turn to a mathematical model.

7.4.1 Mathematical Understanding of the Effects of Supercharging

A change in pressure was seen earlier in Chapter 4, when we discussed general fuel cells. In that case we were only referring to the pressure change from the cathode to the anode. In our specific case there are some necessary modifications, but by starting with the general relationship Eq.(7.3) we will better be able to understand the problem.

$$\Delta V = \frac{RT}{2F} \ln \left(\frac{P_2}{P_1} \right) \quad (7.3)$$

We must recall that this relationship was derived from a logarithmic principle, thus we can modify it to a power equation and say:

$$P_{gain} = C \ln \left(\frac{P_2}{P_1} \right) In \quad (7.4)$$

Unfortunately this is not the only power associated with the system, there is also the power lost due to the need to compress the gasses. By adding this term in we arrive at the total power loss expression, Eq.(7.5)

$$P_{Lost} = c_p \frac{T_1}{\eta_m \eta_c} \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \dot{m} \quad (7.5)$$

where γ is the ratio of specific heat \dot{m} is the mass flow rate η_m is the efficiency of the motor, and η_c is the efficiency of the compressor. It was shown before that \dot{m} is derived from Eq.(7.1). By inserting known values and applying the definition of power we can solve for the total change in voltage.

$$\Delta V_{loss} = 3.58 \times 10^{-4} \times \frac{T_1}{\eta_m \eta_c} \left(\left(\frac{P_2}{P_1} \right)^{.286} - 1 \right) \lambda \quad (7.6)$$

The interpretation of what the values of the constants should be in Eq.(7.6) is the cause for much discrepancy as to what the right answer to the question of what the desired pressure should be. If “optimistic” values are chosen then the peak performance will arrive at a pressure ratio of 3, and it will give a .015V increase per cell. If a more “pessimistic” interpretation of the numbers is used then we find that as the ratio increases the loss is consistently greater, thus determining that pressurization has a negative effect on the cell.

7.5 Conclusion

The PEM offers a perfect stepping stone into the commercialization of fuel cells. They can be operated at low temperatures, thus allowing them to compete in the same market as batteries. And they can be scaled up for larger projects, such as the Ballard Power Systems bus.[9] Since their membrane is a solid-state material the cell can easily be stacked, so long as proper bipolar plate designs are used. The PEM offers a great balance between power and size/operating temperate. They will likely be the fist cells commercialized on a large scale. Fig. 7.4 shows the overall performance of a PEM operating at standard pressure and 60°C.

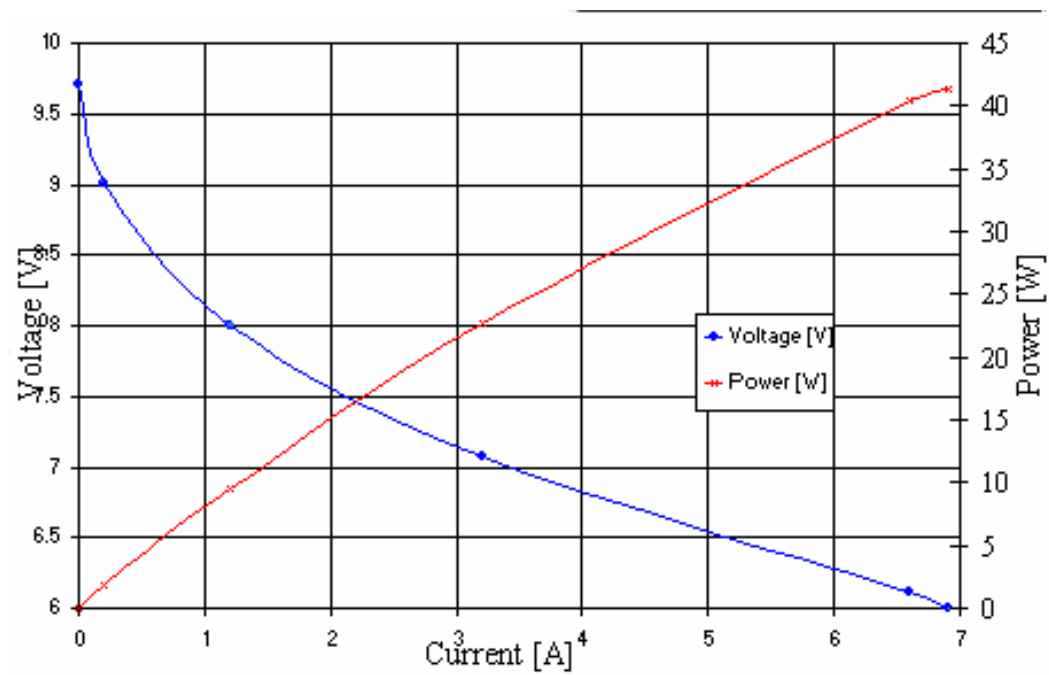


Figure 7.4: Overall Performance

Chapter 8

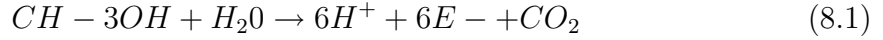
Direct Methanol Fuel Cells (DMFC)

8.1 Introduction

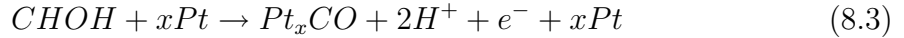
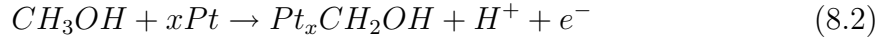
The use of pure hydrogen in fuel cells is not the only way to convert hydrogen into useful electric energy. A variety of reactions can produce hydrogen indirectly, thus enabling the classic hydrogen fuel cell chemical reaction to take place. Since the storage, distribution, and production of hydrogen are tasks that have not been completed yet some members of industry and government have called for alternate sources of hydrogen. Although many options are possible, since hydrogen can be drawn from virtually any hydrocarbon (fossil fuel or renewable fuel), many hold high hopes for the direct use of methanol. Since methanol is a liquid at STP (boils at 65°C and 1 atm) it can easily be stored, in a container like gasoline is, and it can be manufactured from a variety of carbon-based feedstocks such as natural gas, coal, and biomass (e.g., wood and landfill gas). The fuel cell system also has other design advantages over pure hydrogen fuel cells. [7] They eliminate the fuel vaporizer and all the heat sources that are associated with it. This is mainly a consequence of the fact the methanol boils at a low temperature. There is also elimination of complex humidification and thermal management systems, again a consequence of the low operational temperature, and an on-board coolant. The on-board coolant comes in the form of the fuel itself. Since the fuel is a methanol and water combination, typically about 5% water, the design of the fuel storage in the cell also allows for cell coolant. And finally, the dramatically lower size and weight of the overall system is an advantage. All of these characteristics make it a very attractive choice for use in a fuel cell system.

8.2 Description of Operation

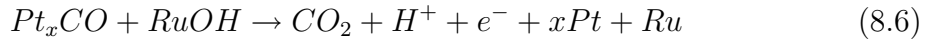
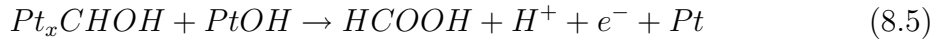
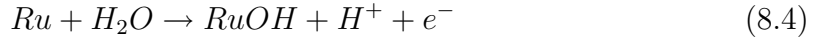
The operation of the whole DMFC system is similar to the operation of the PEM in terms of the physical manufacturing of the cell. The major difference is in the fuel cell supply. The fuel is a mixture of water and of methanol; it reacts directly at the anode according to:



As mentioned above the boiling point of methanol at atmospheric pressure is $65^\circ C$, thus the cells requires an operating temperature around $70^\circ C$ (to avoid a too high vapor pressure). The reaction mechanism is much more complex with the appearance of species adsorbed as well as with HCOH and HCOOH. If one considers this reaction on a Pt/Ru catalyst, it can be represented with the following stages [13]:



The compounds PtCOH and PtCO are poisons for Platinum, and after research it was found that the addition of Ruthenium makes it possible to cure the Pt, and prevent poisoning.



Eq.(8.4) through Eq.(8.6) give the production of the hydrogen, which can in turn be used by the cathode. The cathode undergoes the typical fuel cell reaction with hydrogen combining with oxygen. The total DMFC equation, representing only the initial and final products for both the cathode and anode is as follows:



This corresponds to a theoretical voltage of 1.21 V at STP, obtained from the Gibbs free energy statement. This voltage, as discussed previously in Chapter 4, is dependant on current density. It is subject to the same inefficiency as a hydrogen fed fuel cell. Fig. 8.1 below is an accurate diagram of the fuel cell and its components.

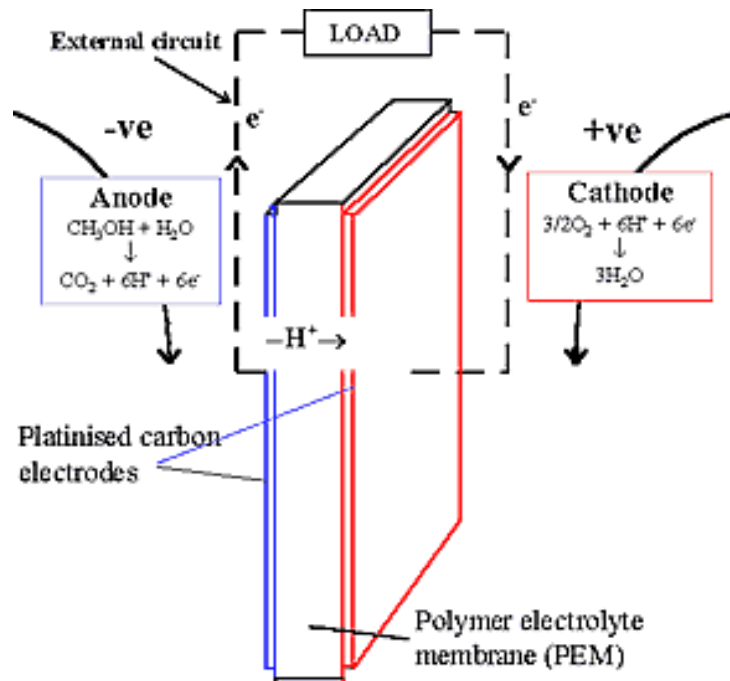


Figure 8.1: Direct Methanol Fuel Cell

8.3 General Voltage Loss Descriptions

8.3.1 Typical Losses

The voltage losses of a DMFC are similar to those associated to a hydrogen-fueled fuel cell. It has activation losses, Ohmic losses, mass transport losses, and fuel crossover losses. These losses are the direct result of several sources of inefficiency in the DMFC. [7]

- the reaction of oxidation is not always complete. There can be formation of acid ($HCOOH$) or formaldehyde ($HCOH$)
- The potentials of electrodes are very different from the theory because of significant over voltage (around 0.3V with the anode and 0.4V with cathode). This is the common fuel crossover loss described in Chapter 4.

The figure below, Fig. 8.2, shows a typical voltage vs. current density for the DMFC. This graph shows that fuel crossover and Ohmic losses are the two major contributors to irreversibility's in the DMFC.

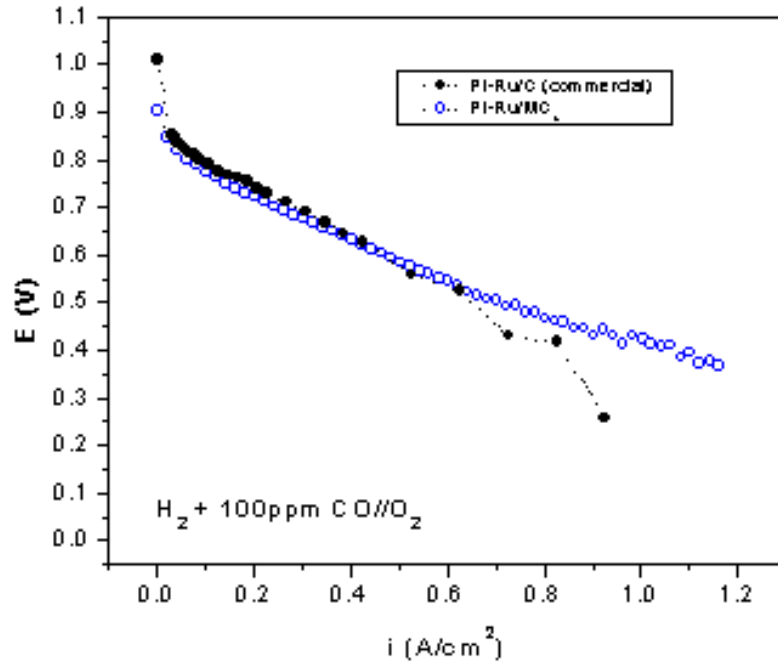


Figure 8.2: Direct Methanol Fuel Cell: Voltage vs. Current Density Plot

The fuel crossover loss occurs for the same reasons that fuel crossover occurs in all types of fuel cells, the inability of a perfect insulator that remains an effective cation transfer medium. Since it is possible to have the fuel leak through the polymer electrolyte and directly combine with the O_2 , there is a constant voltage drop that occurs, even at zero voltage, see Chapter 4. The Ohmic losses that are also present in the methanol fuel cell, are mainly due to the resistances associated with the bipolar plates and the interconnections of the cell stack. These losses are considered to be acceptable in terms of how other fuel cells. The main concern that developers are having is with the anode and cathode.

8.3.2 Anode and Cathode

There are several issues that make the DMFC a less attractive options then the pure hydrogen fuel cell. These problems are those associated with the inability to get full potential out of the anode and the cathode. Three identified problems are as follows [9]:

- Acid electrolytes must be used because carbonate formation is a serious problem in alkaline solution, especially at projected useful current densities. The

corrosive tendency of the acid causes slow kinetics at the cathode

- There have been marked problems with the cathode and the anode having the same electro-catalysts. This results in a situation where it is possible to have “chemical short circuits” thus results in more inefficiencies
- The catalysts are typically high in Pt content, thus making them highly susceptible to poisoning (CO)

8.4 Conclusion

These anode and cathode problems have made industry weary of the DMFC. Since, the solution to the above listed problems have not been completely solved yet, methanol is not in full commercialization. Several companies such as JPL, IFC, and Ballard are trying to solve these problems, thus bringing the cells closer to commercialization. The successive of the DMFC's are varied, but the most important of which is the transcontinental trip by the first DMFC car, completed in June 2002.[7] Other than cars, the DMFC will likely be used in smaller electronics, show below Fig.8.3

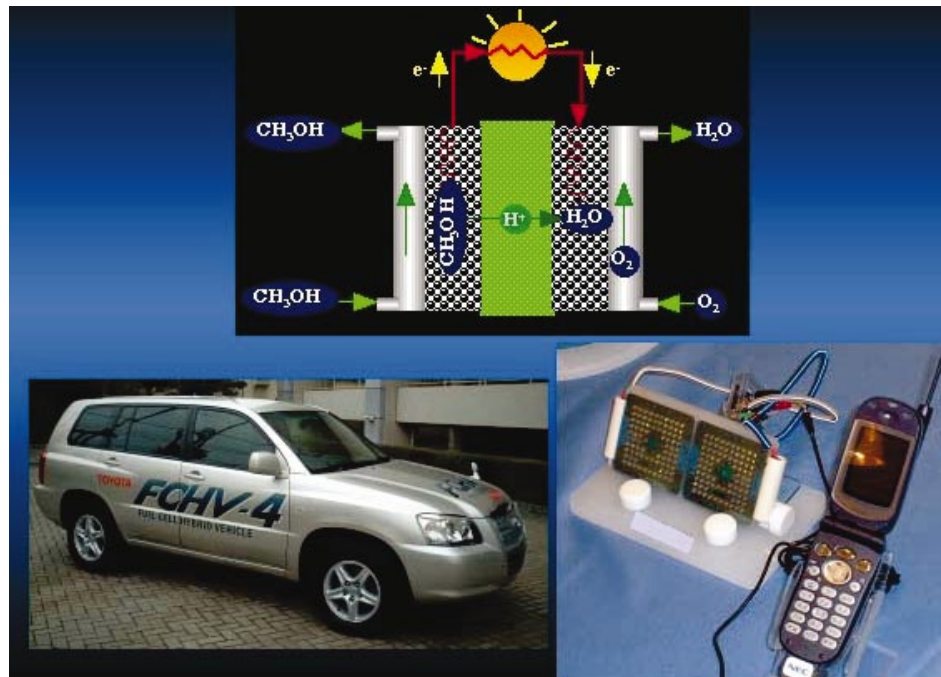


Figure 8.3: Direct Methanol Fuel Cell: Potential Uses

Chapter 9

Phosphoric Acid Fuel Cells

Phosphoric Acid Fuel Cells are much like Proton Exchange Membrane fuel cells. They use a proton-conducting electrolyte. The chemical reactions use highly dispersed electrocatalyst particles within carbon black. The electrode material is generally platinum. An inorganic acid of concentrated phosphoric acid is used as the electrolyte, hence the name of the fuel cell. This electrolyte will conduct protons. The phosphoric acid fuel cell operates at approximately $180 - 200^{\circ}\text{C}$.

9.1 The Electrolyte

Phosphoric acid is used as the electrolyte because it is the only inorganic acid that exhibits the required thermal stability, chemical and electrochemical stability and low enough volatility to be effectively used.[9] Phosphoric acid does not react with CO_2 to form carbonate ions such as the case with alkaline fuel cells; therefore carbonate formation is not a problem with phosphoric acid fuel cells.

The phosphoric acid is uniquely contained in a silicon carbide particle matrix using capillary action. Phosphoric acid has a freezing point of 42°C , which is high compared to electrolyte materials used in other fuel cells. As the electrolyte freezes and expands, it will cause internal stresses in the containment system; therefore to avoid the potential problems associated with these stresses the fuel cell electrolyte is kept at a temperature above 42°C . Small amounts of the acid electrolyte is lost during operation therefore either excess acid should be initially put into the fuel cell or the acid should be replenishable.

The silicon carbide matrix which holds the electrolyte is produced with particles approximately 1 micron in size allowing the matrix to be about 0.1-0.2 mm thick. [9] This thickness allows considerably low ohmic losses. The structural matrix is thick enough to prevent cross over of the reactant gasses from the anode to the cathode.

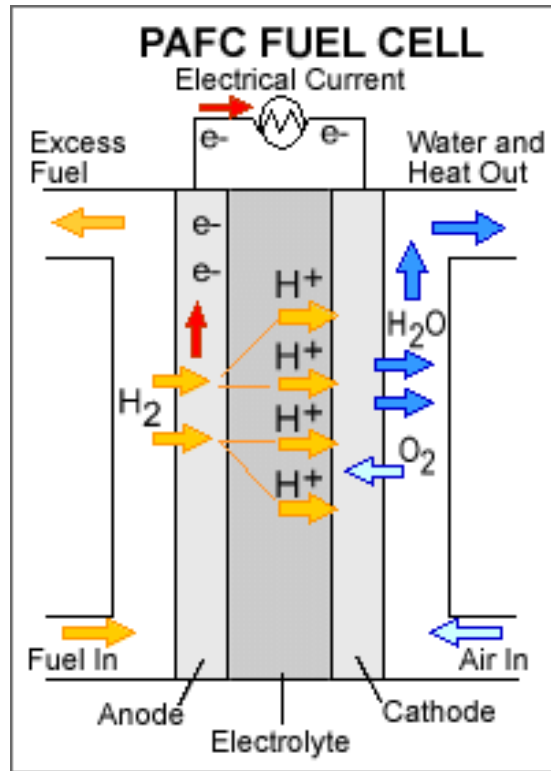


Figure 9.1: Phosphoric Acid Fuel Cell

9.2 The Electrodes and Catalysts

The phosphoric acid fuel cell uses gas diffusion electrodes. The primary catalyst for choice is platinum on carbon. Carbon is bonded with polytetrafluoroethylene (PTFE) to create the catalyst structure. The carbon has some major functions [9]:

- To disperse the Pt catalyst to ensure good utilization of the catalytic metal
- To provide micropores in the electrode for maximum gas diffusion to the catalyst and electrode/electrolyte interface
- To increase the electrical conductivity of the catalyst.

The carbon has allowed a reduction in platinum loading in the development of fuel cells. The current platinum loadings are approximately $0.10 \text{ mg } \frac{Pt}{cm^2}$ in the anode and about $0.50 \text{ mg } \frac{Pt}{cm^2}$ in the cathode.

9.3 The Stack

A stack is used in the structure of a phosphoric acid fuel cell. The stack consists of many cells which contain a ribbed bipolar plate, the anode, electrolyte matrix and cathode. The bipolar plate allows the cells to be connected in series, and allows gas to be supplied to the anode and cathode. It is common for a stack to consist of approximately 50 or more cells which will produce a usable voltage.

Multi-component bipolar plates are currently being used in phosphoric acid fuel cells. These bipolar plates are constructed from layers which allow them to be manufactured more easily and cheaper than previous methods. Bipolar plates used to be made from graphite with machined gas channels on each side. The multi-component plates use a thin carbon plate to separate reactant gasses in neighboring cells and separate porous ribbed plates for gas distribution. This forms a ribbed substrate structure. Advantages of the ribbed substrate are [9]:

- Flat surfaces between catalyst layer and substrate promote better and uniform gas diffusion to the electrode
- It is amenable to continuous manufacturing process since the ribs on each substrate run in only one direction
- Phosphoric acid can be stored in the substrate, thereby increasing the lifetime of the stack

9.4 Stack Cooling and Manifolding

It is essential to remove the heat from the stacks that is created during operation. Two types of cooling can be used. The preferred method of cooling is by using a liquid, and the other is by using gas. Liquid cooling is preferred because the thermal conductivity for water is approximately twenty times higher than that for air, therefore water will extract heat from a system much more effectively than air. The liquid water cooling can be performed using either boiling water or pressurized water. Boiling water is quite effective in creating uniform temperatures throughout the stack. This temperature uniformity causes an increase in the cell efficiency.

As with any liquid water cooled systems, problems arise that must be designed around to avoid. Water treatment is required to filter and purify the water to minimize corrosion, wear and buildup in the piping system. The addition of a water filtration system increases the cost of the fuel cell therefore generally water filtration is only used in fuel cells greater than 100 kW.

Manifolding is important to optimize the gas supply to the cells. Generally external manifolds attached to the outside of the stacks are used. Manifold design

allows the fuel gas to be supplied uniformly to each cell. Reducing temperature gradients will reduce thermal stresses and therefore increase the lifetime of the fuel cell. Just the same as alkaline fuel cells, if the phosphoric acid fuel cell is operated at high pressure then the whole fuel cell is placed within a vessel of nitrogen which is at a higher pressure than that of the fuel cell to ensure that no gasses leaking out of the fuel cell could cause harm or safety risks.

9.5 Operating Pressure

As with all fuel cells discussed thus far, the cell performance is determined by the pressure, temperature, reactant gas composition and utilization. As was shown in Ch. 2 the performance of a fuel cell increases with increasing pressure. The voltage also increases with pressure due to the relationship given in Chapter 3:

$$\Delta V = \frac{RT}{4F} \left(\frac{P_2}{P_1} \right) \quad (9.1)$$

But it has been shown that the Nernst voltage given in Eq. (9.1) does not fully describe the voltage gain at higher pressures. The increased pressure decreases the activation polarization at the cathode, because of the increased oxygen and product water partial pressures. If the partial pressure of the water is allowed to increase, a lower phosphoric acid concentration will result. This increases ionic conductivity and in turn increases current density. The increased current density reduces ohmic losses. As a result of the lower phosphoric acid concentration the actual voltage gain is much higher than that described by the Nernst voltage equation. According to Hirschenhofer the actual voltage gain is:

$$\Delta V = 63.5 \ln \left(\frac{P_2}{P_1} \right) \quad (9.2)$$

9.6 Temperature Effects

As has been shown in the previous fuel cells, the reversible voltage decreases at the temperature increases. The maximum decrease is approximately $0.27 mV/^{\circ}C$ for phosphoric acid fuel cells. As shown in Chapter 4 an increase in temperature has a beneficial effect on cell performance because activation polarization, mass transfer polarization, and ohmic losses are reduced. Hirschenhofer has shown that at a mid-range operating load ($250 \frac{mA}{cm^2}$) the voltage gain with increasing temperature of pure hydrogen and air is given by:

$$\Delta V_T = 1.15 (T_2 - T_1) mV \quad (9.3)$$

This is reasonable for a temperature range of $180 < T < 250^{\circ}C$. [9]

9.7 Research and Development

Phosphoric acid fuel cells were the first commercially available fuel cells. Many PAFCs have operated for years upon which much knowledge and technological improvements have been made. The reliability of the stack and the quality of the power produced have been greatly improved. Currently there are a total of approximately 65 MW of phosphoric fuel cells in use or being tested. International Fuel Cells and Toshiba for Tokyo Electric Power has created the largest phosphoric acid fuel cell power plant capable of supplying 11 MW of grid quality AC power. [13]

Unfortunately the cost of technology is still too high to be economically competitive with alternative power generation systems. Research is being directed to increase the power density of the cells and reduce costs which both affect each other.

Chapter 10

Solid Oxide Fuel Cell (SOFC)

10.1 Introduction

Solid Oxide Fuel Cells have become a valid option for energy generation due to their attractive features. These cells, part of the broader category of ceramic fuel cells, are attractive due to their solid-state components. These cells, unlike the high temperature MCFC, have a solid-state electrode, as well as a solid-state anode, cathode, and cell interconnects. The government has become very interested in this type of fuel cell, since it conforms well to their plan of a solid state energy source fueled by hydrogen, as described by the SECA. Besides being a fuel cell that fits well into the governments energy plan, there are also many positive features that it has in its own right. Due to its high temperature of operation, 1000°C , it is an effective source of byproduct heat which can be used for cogeneration. The SOFC can also be manufactured in any manner of configurations; this is a consequence of its solid-state design. Due to the high temperature of operation it does not require precious metals on the anode or cathode, *Ni* ceramics and Lanthanum Manganite are typically used as the anode and cathode, respectively. And finally, the ability to use a wide variety of fuels makes the SOFC a promising technology. Since the SOFC operates at high temperatures is able to use pure H_2 and CO . Since the materials are not easily poisoned it is also possible to use methane, diesel, gasoline, or coal gas. Although its operational temperature makes it impractical for smaller applications, i.e. hand-held devices, the SOFC in general is a very promising fuel cell for use in the distributed or centralized power generation industry.

10.2 Configurations

Since the SOFC is made entirely of solid-state components it is possible to manufacture them in a wide variety of configurations. Although the geometry of the cell varies by company all types of cells operate with common components. Each geometric configuration has its advantages and disadvantages. The first cell developed was the planer fuel cell. This cell soon found dramatic limitations in the manufacturing process. At the time it was very difficult to form large flat plates that could adequately seal gas, this was a problem due to the high temperature of operation. To relieve these problems the industry decided to experiment with other geometric configurations. An option to alleviate the need for a gas seal was incorporated in the design of the tubular SOFC, and the bell and spigot configurations. These cells have overlapping components, and thus remove the issue of having adequate gas seals. Although all three types of cells are being researched today, the tubular and the cylindrical, SOFC has proven to be the most advanced and efficient designs.

10.2.1 Planer

The planar SOFC was the first geometry attempted for the SOFC, since its application is widely used in PAFC and MCFC. This design is very advantageous since it is used simple cell interconnects and is easily stackable. Although it has many advantages it was discovered early on that gas leaks at the higher temperature are a formidable design challenge, as well as thermal mismatches. This design offers improved power density relative to the tubular and bell and spigot designs, but at the price of high temperature gas seals. These seals are possible to manufacture, typically a compressive thermal seal, but the non-uniform stress that is induced by the compressive seal is seen as a barrier to the design. Since the ceramics are very weak in tension, it has been shown that the cells break down due to thermal fatigue after several cycles. Some research has also indicated that the use of a compressive seal may inhibit the height of the overall stack. This problem most likely will occur since as the stack increases in size there is a greater probability that the thermal stress induced between any two cells will exceed tolerances. The fabrication techniques for the planar type fuel cell are a well-understood processes, and are relatively cheap and easy to perform. The description for manufacturing processes will be discussed later in section 4. The planar fuel cell has become more popular recently due to the advances in manufacturing processes; this motivation is partially supplied by government funding.

10.2.2 Tubular

The tubular configuration of the SOFC is the most advanced of the major geometries being researched right now. Its unique configuration eliminates the need to design gas seals. These cells do come at a cost unassociated with the other types of cells, and that is the increased Ohmic loss. Since the tubular design forces the electrons to travel along a much longer path than most other fuel cells, the losses due to interconnect resistance are significant, see Fig. 10.1. The Siemens design is formed by extruding the cathode, and then through a variety of manufacturing processes building the other layers around the cathode. Thus the cathode serves not only as the structural base of the cell, but also as the site for oxidation of the oxygen in the air stream. This process greatly simplifies the manufacturing process of making large cells, currently they are 150cm in length. The cathode tube is closed at one end; this eliminates the need for a gas seal, since it is geometrically separated. The fuel gas flow on the exterior of the tubes, is in a co flow direction, see Fig. 10.1

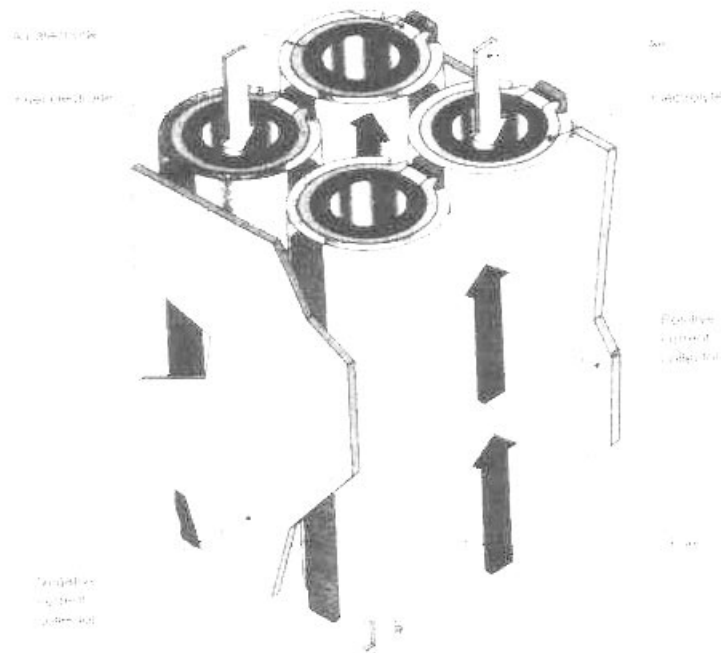


Figure 10.1: Fuel can oxygen flow in a Tubular SOFC

As mentioned above the solution that fixed the problem of gas seals at high temperature created a separate problem. This is the long current path that the electron must follow, see Fig. 10.2. Although the Ohmic losses in all fuel cells are

a source of loss, they are especially apparent in the tubular SOFC. This problem is being faced as a materials and design problem. As the cells become smaller and better materials are used the loss due to this long current path will drop.

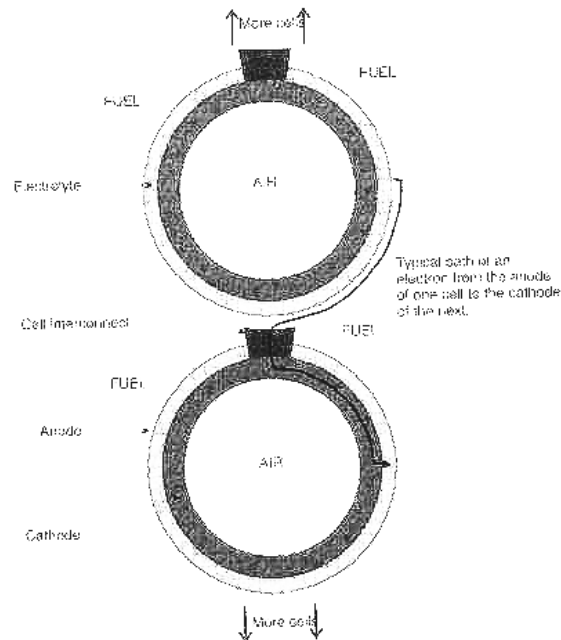


Figure 10.2: Path of the electron in a Tubular SOFC, Siemens Westinghouse design

10.3 Cell Components

Although there are several configurations for the SOFC the planer and tubular type are dramatically more advanced. Siemens Westinghouse currently has multiple units being tested in the field. They are technically sound and feasible sources of energy generation, but unfortunately they are hampered by high capital cost, and thus are not ready for commercialization. The design is still in testing, and all the material issues have not been worked out yet, and as a result the cells currently being tested are yielding lower than expected performances, and are dramatically more costly compared to other competitors. Currently the cost of raw materials for the tubular design cost about $\$7/kW$, where as manufacturing cost are nearly $\$700/kW$. When these prices are compared to the total cost of an operational ICE, which costs $\$60/kW$, it is obvious that improvements need to be made in order for the SOFC to have any

significant market penetration. Below is a list of the advancements made since the beginnings of SOFC research in the material of the cell.

Component	1965	1975	2000
Anode	Porous Pt	Ni/ZrO_2 cermets	YSZ
Cathode	Porous Pt	Stabilized ZrO_2	Doped Lanthanum Manganite
Electrolyte	Yttria Stabilized ZrO_2	YSZ	YSZ
Cell Interconnect	Pt	Mn (Cobalt Chromate)	Doped Lanthanum Chromate

Table 10.1: The Evolution of Cell Components (Specifications from the Siemens Westinghouse)

Currently the work that is being considered for the cell is in developing mechanically tough materials, thus providing a base for which planer fuel cells can be built upon. If such a component is found it will greatly reduce the problems caused by the high and uneven thermal and mechanical stresses. This component would also have to have an equivalent thermal expansion coefficient. Recently, December 2002, Lawrence Berkeley National Laboratory scientists developed a solid oxide fuel cell (SOFC) that promises to generate electricity as cheaply as the most efficient gas turbine. Their innovation lies in replacing ceramic electrodes with stainless-steel-supported electrodes that are stronger, easier to manufacture, and, most importantly, cheaper. This latter advantage marks a turning point in the push to develop commercially viable fuel cells. This potential breakthrough could break the \$400/ kW mark set by the SECA. The final design of the fuel cell system is not complete yet, but engineers involved say the cost will be close to \$400/ kW . [13] The electrode of the fuel cell is currently Yttria stabilized Zirconia, YSZ. The current drive is to potentially add Al_2O_3 to the electrode matrix in the hope of adding strength. This is a very important concept that needs to be designed and developed if the planer SOFC is to be a viable option. The increased strength will be approximately from 300 MPa to 1200 MPa . This did increase the general resistivity of the cells stack, but it was not a severe loss of potential. [13] The final and most important step that will reduce cost for the SOFC will be the reduction of manufacturing, as mentioned above. The processes are described below and are currently being heavily researched by Siemens, who hopes to be able to manufacture all components by PVD, particle vapor deposition which is a cheap and effective manufacturing process.

10.4 Manufacturing Techniques

10.4.1 Tape Casting

Tape casting is a suitable processing technique to produce thin ceramic sheets with smooth surfaces and a very precise dimensional tolerances.[7] The casting is performed by applying a ceramic slip, cut by a sharp blade, and extruded onto a temporary support. The ceramic is then dried and then can be shaped into its final form. Tape casting of a self-supporting structure costs \$1/kg, and has a thickness of $200\mu m$. The can be formed as thin as $2\mu m$, if a non-self supporting application is necessary.

10.5 Performance

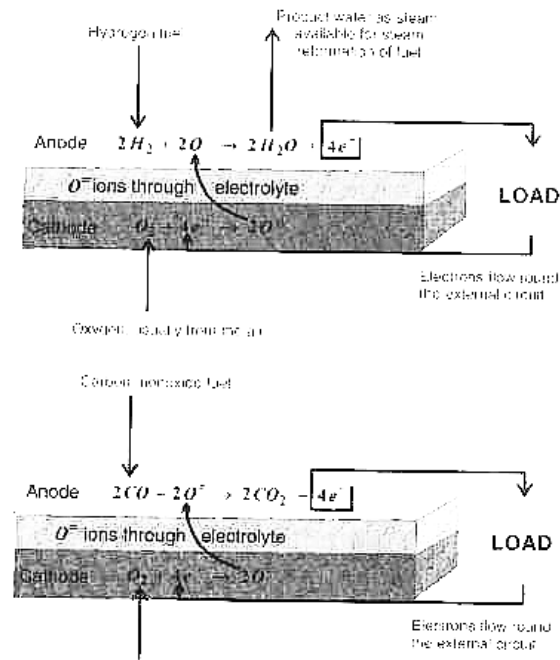


Figure 10.3: Basic Chemistry associated with a SOFC

The SOFC, like the MCFC, is a high temperature fuel cell, but unlike the MCFC is not susceptible to a wide variety of contaminants. This comes at a cost, it has a lower open circuit voltage as compared to the MCFC. The overall losses of the SOFC are mainly those associated with Ohmic losses. Since the cell operates at high temperatures it has almost no activation losses, and the usefulness of the cell is not

in the range of mass transportation losses. The basic fuel cell equation derived in Chapters 2 and 3 apply to the SOFC. A list of these important equations are listed below.

$$E = \left(\frac{RT}{2F} \right) \ln \frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \quad (10.1)$$



As seen by Eq.(10.1) the change in pressure and an increase in temperature will be significant to maximizing the potential of the SOFC. As mentioned previously, Ohmic losses are a very big concern in the SOFC. According to information gathered by the Department of Energy the Ohmic breakdown is as follows: 45% cathode, 18% anode 12% electrolyte and 25% interconnect. When the length of electron path and resistivity of the material are considered, almost 80 % of the loss is in the cathode. The cathode supplies so much resistance mainly due to the long electron path.[13] The figure 10.2 below shows the long electron path.

10.5.1 Effects of Pressure

The pressure differential across the cell will have a dramatic effect on the cell. Siemens demonstrated that their tubular design can operate at .65V and 500 $\left[\frac{mA}{cm^2}\right]$ at a pressure of 10 atm. This is a dramatic increase from 1 atm, where the cell only operates at .47V at the same current density. It has been shown that Eq.(10.5) is a reasonable source for determining the effects of an increased pressure.[13] It should be noted that there are conflicting views about the pressure-reduced constant.

$$\Delta V(mV) = 59 \log \left(\frac{P_2}{P_1} \right) \quad (10.5)$$

10.5.2 Effects of Temperature

As noted by the Nernst equation for a SOFC, Eq.(10.1), and increase will have a dramatic effect on the SOFC. First and foremost the cells must operate at a high temperature or else the solid-state ceramic will not conduct the oxygen through its membrane. Once the cell is at a sufficient temperature to allow transport, around

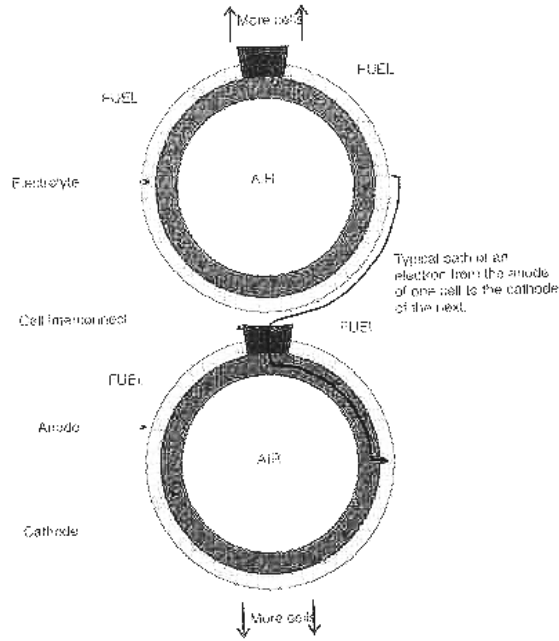


Figure 10.4: Path of the electron in a Tubular SOFC, Siemens Westinghouse design

800°C , the effects of a temperature increase are dominated by the Nernst equation and the current density. Again like the effects of pressure, the effect of temperature is not completely understood, and so the following equation is only a current conjecture.

$$\Delta V(\text{mV}) = K (T_2 - T_1) J \quad (10.6)$$

where K is defined in Table 10.2 and J is the operational current density.

10.5.3 Effects of Impurities

As mentioned in the introduction to SOFCs, one of the advantages to a SOFC is its resistivity to impurities. This is very important to a fuel cell that will most likely be used in a non-portable application. Coal gas is readily available and can be used in the SOFC. The three impurities of potential concern are ammonia, NH_3 , hydrogen chloride, HCl , and hydrogen sulfide, H_2S . These are all common impurities that had to be scrubbed in other fuel cells, MCFC. In testing it was found that 5000 ppm of NH_3 had no effect on the fuel cell. A source of 1 ppm of HCl was then added and again no loss was detected, but with the addition of 1 ppm of H_2S the system dramatically lost potential (close to .11 V initially). After the initial loss of voltage

K	Temp ($^{\circ}C$)
0.003	950
0.006	1050
0.008	1000
0.009	800 - 900
0.014	900 - 1000
0.068	850

Table 10.2: K values for Temperature Dependence

the system continued to decline in potential in a linear digression, with a slope of .0054 V per 400 hrs of operation. Thus a SOFC would have to be scrubbed of the H_2S content. The follow up to the previous experiment determined that .5 ppm was an acceptable level.[13]

10.6 Conclusion

The SOFC is a very technically sound design that has the potential to deliver power to a multitude of stationary locations. It has the ability to supply excess heat to a boiler and thus have an even greater efficiency. The variety of fuels that can be used with the SOFC is very wide, and will no doubt contribute to its attractiveness on the open market.

Part II

Fuel Cell Applications and Research

Chapter 11

Fuel Cell System Components

For fuel cells to function efficiently, air must be circulated through the fuel cell for cooling and cathode reactant supply. To accomplish this, compressors, turbines, ejectors, fans, blowers and pumps are used. The exhaust gas from fuel cells can also be used by turbines to create additional usable power and therefore increase the efficiency of the fuel cell.

11.1 Compressors

There are four major types of compressors that can be utilized in a fuel cell system. These include the Roots compressor, the Lysholm or screw compressor, the centrifugal or radial compressor, and the axial flow compressor.[9] Each has its own advantages and disadvantages for various fuel cell types.

The Roots compressor is cheap to produce and works over a wide range of flowrates. A disadvantage is that it only gives useful efficiencies over a small pressure difference. Improvements in this type of compressor have been developed by Eaton Corporation. Though, the Roots compressor is still only useful for small pressure changes of about a 1.8 factor increase in pressure which is quite small.[9]

The Lysholm or screw compressor works by two screws which counter rotate driving the gas between the two screws forward and therefore compressing it. There are two configurations for the screw compressor. In one, an external motor drives only one rotor, and the second rotor is turned by the first, but this contact must be lubricated with oil. This is unfavorable for fuel cells because the oil can enter the fuel cell. The second configuration uses a synchronizing gear to connect to two screws. The screws do not come in contact with each other, therefore no oil is needed and this type of compressor is favorable for fuel cell systems because it does not introduce oil into the fuel cell. The advantage of the Lysholm compressor is that it can provide

a wide range of compression ratios. It can increase the pressure up to eight times the input pressure. The drawback to these types of compressors is the cost because they are quite expensive to manufacture.[9]

The centrifugal compressor is the most common type of compressor. The centrifugal compressor uses kinetic energy to create a pressure increase. This type of compressor is commonly found on engine turbocharging systems. It is relatively low cost and the technology is mature. This type of compressor is also available to suite a wide range of flowrates. A disadvantage is that it cannot be operated at low flowrates. Another problem is the operational rpm of this compressor. Typical operating speeds are approximately 80,000 rpm.[9]

The axial flow compressor uses large blades to push air through a device with a decreased cross sectional area. One can think of this compressor as the inverse of a turbine. Axial flow compressors are expensive to manufacture, yet the efficiency is high over a very limited range of flowrates. According to Watson, 1982, these types of compressors will most likely only be used for systems above a few MW to make them worth while.[9]

11.2 Compressor Efficiency

Compressor efficiency is important to define because it plays an important role in the overall efficiency of the fuel cell. The efficiency of the compressor is found by using the ratio of the actual work done to raise the pressure from P_1 to P_2 to the ideal work that would be performed if the process had been reversible or isentropic.

In a reversible adiabatic process the pressure change of the gas is related to the temperature change through the relationship [9]:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (11.1)$$

where T_2 is the isentropic temperature, and γ is the ratio of the specific heat capacities of the gas, C_p/C_v . To find the actual work and the isentropic work done, some general assumptions are made [9]:

- The heat flow from the compressor is negligible
- The kinetic energy of the gas as it flows into and out of the compressor is negligible, or at least the change is negligible
- The gas is a perfect gas, and so the specific heat at constant pressure, C_p is constant.

The actual work done by the system is therefore:

$$W = c_p(T_2 - T_1)m \quad (11.2)$$

where m is the mass of the gas compressed, T_1 and T_2 are the inlet and exit temperatures respectively, and c_p is the specific heat at constant pressure. The isentropic work done by the system is therefore:

$$W = c_p(T_2 - T_1)m \quad (11.3)$$

where T_2 is the isentropic temperature given by Eq. (11.1). The efficiency is the ratio of these two quantities of work.

$$\begin{aligned} \eta &= \frac{\text{isentropic work}}{\text{real work}} = \frac{c_p(T_2 - T_1)m}{c_p(T_2 - T_1)m} \\ \text{and } \eta_c &= \frac{T_2 - T_1}{T_2 - T_1} \end{aligned} \quad (11.4)$$

Substituting Eq. (11.1) into the above equation we get:

$$\eta_c = \frac{T_1}{(T_2 - T_1)} \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (11.5)$$

The change in temperature can be found from the above equation:

$$\Delta T = T_2 - T_1 = \frac{T_1}{\eta_c} \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (11.6)$$

There are also losses due to friction within the bearings of the rotating shaft which must be accounted for. The total efficiency is therefore the compressor efficiency times the mechanical efficiency of the shaft or:

$$\eta_T = \eta_m \times \eta_c \quad (11.7)$$

11.3 Compressor Power

We can use Eq. (11.2) to determine the power that would be required to increase the temperature of the gas. Since power is defined as:

$$\begin{aligned} \text{Power} &= \frac{\text{Work}}{\text{time}} \\ \dot{W} &= c_p \Delta T \dot{m} \end{aligned} \quad (11.8)$$

Substituting Eq. (11.6) into the above equation we arrive at:

$$Power = c_p \frac{T_1}{\eta_c} \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \dot{m} \quad (11.9)$$

The isentropic efficiency, η_c , is readily found from efficiency charts. One must remember to take into account the mechanical efficiency of the compressor when finding the power needed from the motor or turbine to drive the compressor. Generally 0.9 is used.

11.4 Turbines

The hot gas exhausted by fuel cells can be harnessed into mechanical work through the use of turbines. The efficiency of a turbine determines whether or not it is economically viable to incorporate into the fuel cell system. The efficiency of a turbine is similar to that of the compressor. Using Eq. (11.1)

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (11.10)$$

and noting that the isentropic temperature T_2 is actually lower than the actual exit temperature the efficiency of a turbine is therefore:

$$\eta_c = \frac{\text{actual work done}}{\text{isentropic work}} \quad (11.11)$$

Substituting in the proper equations as we did for the compressor, the efficiency becomes:

$$\begin{aligned} \eta_c &= \frac{T_1 - T_2}{T_1 - T_2} \\ &= \frac{T_1 - T_2}{T_1} \left(1 - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \end{aligned} \quad (11.12)$$

and the temperature change can be found to be:

$$\Delta T = T_2 - T_1 = \eta_c T_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (11.13)$$

as the same with the compressor, we can find the power from:

$$\begin{aligned}
Power &= \frac{Work}{time} \\
\dot{W} &= c_p \Delta T \dot{m} \\
Power, \dot{W} &= c_p \eta_c T_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \dot{m}
\end{aligned} \tag{11.14}$$

Again we note that the power available to drive an external load is found by multiplying the above power by η_m , the mechanical efficiency.

11.5 Ejector Circulators

The ejector is the simplest pump. There are no mechanically moving parts. Hydrogen fuel cells that use pressurized stored hydrogen use these types of pumps. Basically ejector circulators use the stored mechanical energy in the pressurized gas to circulate the fuel around the cell.

11.6 Fans and Blowers

An easy and economical way to cool a fuel cell is to use fans and blowers. A common fan such as the axial fan is effective in moving air over parts, but is not effective across large pressure differences. The typical back pressure for this type of fan is approximately 0.5 *cm* of water which is very low. Therefore these types of fans are suitable for a few very open designs of PEM fuel cells.[9]

Greater pressure differences can be obtained using the centrifugal fan. These types of fans draw air through the center and force it outward creating a pressure rise. Centrifugal fans are mainly used for circulating cooling air through small to medium sized PEM fuel cells. Even though centrifugal fans can create greater pressure compared to the axial fan, the pressure is still only 3 to 10 *cm* of water which is quite low.[9] It is helpful to note the efficiency of a cooling system is:

$$Cooling\ system\ effectiveness = \frac{rate\ of\ heat\ removal}{electrical\ power\ consumed} \tag{11.15}$$

11.7 Membrane/Diaphragm Pumps

As we have seen in the discussion of PEM fuel cells, small to medium sized PEMs are expected to be a substantial sized market for portable power systems. The problem

with the cooling of PEMs is the closed system cooling. Closed system cooling in small to medium sized PEMs creates back pressure of about 10 kPa or 1 m of water. Obviously this is too high for axial or centrifugal fans as discussed earlier. Therefore diaphragm pumps are ideal for such situations. These types of pumps are readily available for gas sampling equipment, small scale chemical processing, and fish tank aerators. Some major features of such pumps are the low cost, silent, reliability, operational pressure, variety of sizes and efficiency. The larger diaphragm pumps can be operated against a back pressure of one to two meters which is ideal for small to medium sized PEMs.[9]

Chapter 12

Fueling the Hydrogen Fuel cell

12.1 Introduction

All of the fuel cells previously discussed use hydrogen as their source of fuel. Although there has been some discussion about the use of methane and CO , these two sources are simply hydrogen carriers. Through reactions within the fuel cell system these are converted in to the necessary hydrogen. Thus the necessary question becomes, where do we get the hydrogen. The sources are hydrogen are vast, being the most abundant element in the universe, despite this abundance it does not appear naturally in a useful form. Currently most hydrogen in the United States, and about half of the world's hydrogen supply, is produced through the steam reforming of natural gas. Although natural gas will likely provide the earliest affordable feedstock for hydrogen, today's costs are prohibitively expensive [13]. Since this is not an economically viable source of producing hydrogen there is research being conducted to develop alternate methods of hydrogen production, see Fig. 12.1.

In the short term, the next 20 to 40 years, hydrogen will likely be produced from fossil fuel sources. The long-term solution to hydrogen production will likely be in production through biological, nuclear, or biomass sources. Despite this research, hydrogen is still expensive and a pollution creating process. As noted by the Department of Energy, today's electrically produced hydrogen costs around \$30 per million British thermal units (Btu); by comparison, natural gas costs about \$3 per million Btu, and gasoline costs about \$9 per million Btu. So the economic barriers to hydrogen production are formidable. [13] Below is a table of common hydrogen carriers. These carriers are either natural sources of hydrogen or are produced through a variety of industrial processes. The following table, see Table 12.1, will describe the common and useful properties of hydrogen rich carriers of hydrogen.

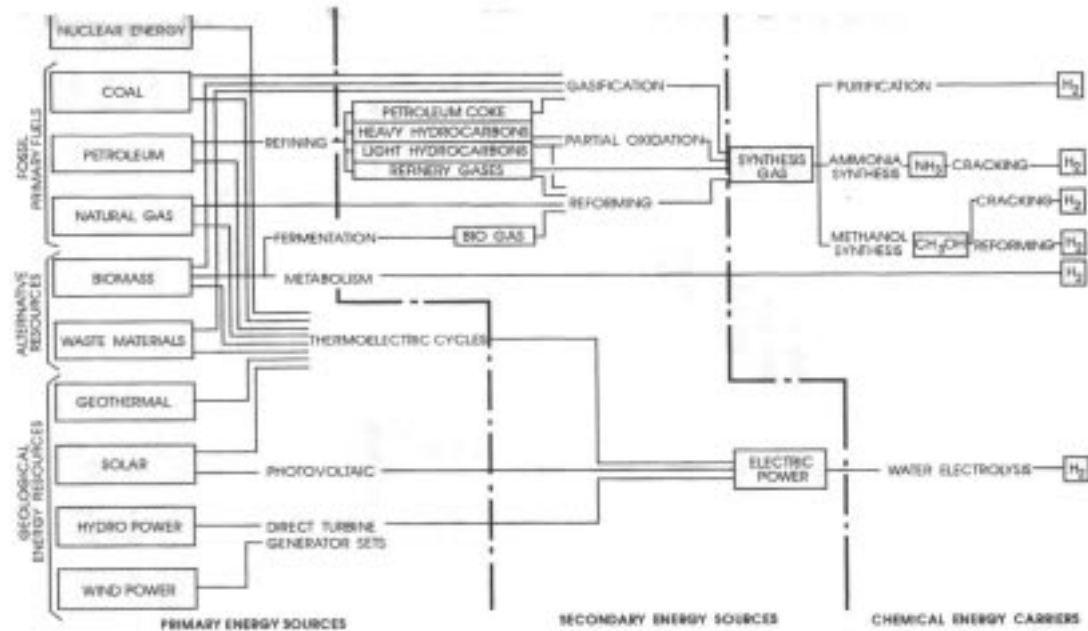


Figure 12.1: Method of possible Hydrogen Production

12.2 Hydrogen Production from Natural Gas

Since hydrogen is currently produced in industry for a variety of reasons, and occasionally as a byproduct of other processes, there is a relevant body of information on how to obtain hydrogen. On such process is the steam reforming of natural gas. In this process the hydrocarbon and steam are run through a catalytic cycle where hydrogen and carbon oxides are released.[7] This method of hydrogen formation is most efficiently used with light hydrocarbons such as methane and naphtha. The steps of this process are outlined in a general form as follows [7]:

- synthesis-gas generation
- water-gas shift
- gas purification

A simple block diagram of the process is shown in Fig.12.2. In the diagram it should be noted that there is a desulphurization process. This is a requirement of the fuel cells. As noted in many of the cells, especially the low temperature cells, sulphur, in

	H_2	CH_4	NH_3	CH_3OH	C_2H_5OH	C_8H_{18}
Molecular Weight	2.016	16.04	17.03	32.04	46.07	114.2
Freezing Point ($^{\circ}C$)	-259.2	-182.5	-77.7	-97.8	-117.3	-56.8
Boling Point ($^{\circ}C$)	-252.77	.161.5	-33.4	64.7	78.5	125.7
Enthalpy (@25 $^{\circ}C$) (kJ/mol)	241.8	802.5	316.3	638.5	1275.9	5512.0
Heat of Vaporisation (kJ/kg)	445.6	510	1371	1100	855	368.1
Liquid Density (kg/l)	77	425	674	792	789	702

Table 12.1: Properties of Hydrogen Rich Fuels

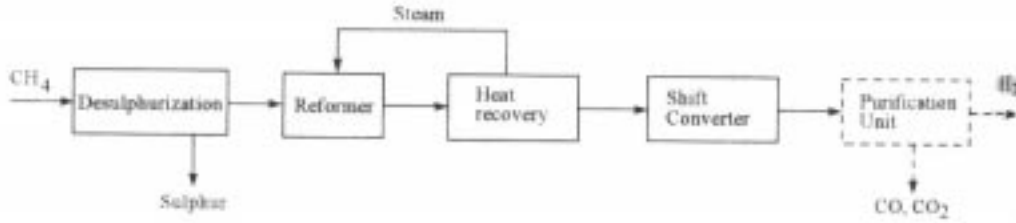
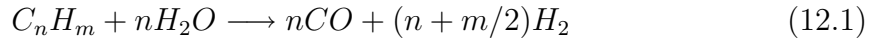


Figure 12.2: Steam Reforming Cycle

the form H_2S was a major inhibitor of performance, this issue is discussed later in the chapter (see Coal Gasification). The overall ideal reformer process is governed by the following equations.



The values of n and m in the preceding equation are the subscripts found in Table 12.1 for carbon and hydrogen combinations. By summing the enthalpy of Eq.(12.1),Eq.(12.2, and Eq.(12.3) we find that the overall reaction is endothermic, thus requiring external energy to be supplied to the system. By heating the process at about $800^{\circ}C$ the conversion of methane is about 98%, and the hydrogen production is about 72%.[7] To supply the heat to the system a reforming furnace must be used. There are three major types used in industry. Each type has certain advantages and thus vary in cost depending on the quality of hydrogen, and the quality of exit gas.

The three types are top-fired furnace, bottom-fired furnace, and the side-fired furnace. The top fired furnace is a good option for most uses since it is smaller in size than the other two types of furnaces, and is economically more affordable. Its operation is such that there is concurrent flow of the inlet gas (providing the necessary heat) and the natural gas (typically methane). This design is intended to provide the most energy to where the endothermic reaction is taking place. Thus maximizing the area of heat transfer. The second type, the bottom-fired furnace, is characterized by counter current flow. This configuration allows for the greatest heat fluxes, and thus heat transfer, to be obtained at the bottom of the furnace. This is necessary when high levels of hydrogen are to be extracted from the natural gas. Since as the natural gas leaves the reformer it sees the highest temperature, thus it extracts the most H_2 . This process is not well suited to materials that are economically available. The uneven heating distribution causes high temperatures in the material and thus can crack the layer separating the gas streams, unless ceramic layers are inserted to protect against the high temperature. The final type of furnace is the side-fed furnace. This design offers the advantage of even heat fluxes, at the expense of multiple burners. Since the two previous types have only one burner, either at the bottom or top, this design has multiple burners all long the reforming tube. Although the heat flux is consistent, it again has heating design considerations. Since the gas increases in temperature along the tube, yet is still being heated at a constant rate the gas temperature is the hottest at the exit. Thus once again the designer must use materials that can handle these high temperatures, or use a lower overall temperature, which means less overall hydrogen is being extracted.

12.3 Hydrogen Production from Coal Gas

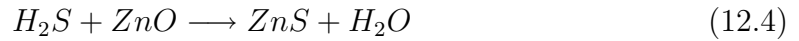
Since MCFC and SOFC operate at a very high temperature ($1000^{\circ}C$) it is natural to use hydrogen produced by coal gasification. Coal is a nonrenewable resource, but it is very abundant, and has well know properties. This source of hydrogen production is also a potentially huge market considering that the US government has decided to take a clean coal approach to energy conversion. This is mainly because the US owns a large amount of coal, and thus it can be mined cheaply. In coal gasification coal is burned and then the reactant gasses are combined with steam, which is produced by the burning coal. This mixture of coal and steam goes through a series of chemical reactions to produce hydrogen and carbon dioxide. This process requires a very high temperature for the rate of reaction to be sufficient, thus its use with MCFC and SOFC. It is also an endothermic reaction, with an enthalpy of 131.8 kJ/mol . The following table has the overall reaction along with the intermediate reactions that occur in a typical coal gasifier.

Reaction	Enthalpy (kJ/mol)
$C + .5O_2 \rightarrow CO$	-110.6
$C + O_2 \rightarrow CO_2$	-393.8
$C + H_2O \rightarrow CO + H_2$	131.4
$C + 2H_2O \rightarrow CO_2 + 2H_2$	96.7
$3C + 2H_2O \rightarrow 2CO + CH_4$	185.5
$2C + 2H_2O \rightarrow CO_2 + CH_4$	12.1
Overall Reaction	
$C + H_2O \rightarrow CO + H_2$	131.38

Table 12.2: Chemical Processes in an ideal Coal Gasifier

Since coal is not perfect carbon there is deviation from this process, this deviation varies according to where the coal came from and what the quality of the mined coal is. The presence of ash, sulphur content, and the tendency to agglomerate make the coal gasification process very difficult and complex, thus inhibiting the efficiency.[7] Just like the natural gas reforming process there are several industrial processes for coal gasification. The basic types of reformers used are: fixed bed, fluidized bed, fast fluidization, and molten bat. Various companies that produce hydrogen use one of these four processes.

Regardless of the process used to create the hydrogen there are some general problems that must be overcome. The most significant is desulphurisation, since coal often has high sulphur content. Since all fuel cell types are extremely sensitive to sulphur compounds, especially the presence of the acid H_2S , it is necessary to remove sulphur from the exit stream. Sulphur removal is also important for natural gas reforming as well. Although there are a variety of processes to remove H_2S , the most common is the use of zinc oxide.[7][9] In this reaction the exit gas is run over a zinc oxide surface, see Eq. (12.4).



This process is typically run at $400^\circ C$ in order to optimize the rate of reaction. A second technique is to inject an absorbent into the exit gas stream. This internal removal process uses limestone ($CaCO_3$), which is relatively inexpensive, to absorb the sulphur. Although this process is possible it does not typically yield a lower H_2S count than external reforming, and this process directly related to the coal feed and the specific gasifier.[7]

12.4 Hydrogen Production from Bio Fuels

A bio fuel is any fuel that is derived from a natural organic material. this can include plant mass, animal waste, and animal tissue. Some of the most important, and abundant sources of bio fuels are: wood, algae, vegetable mass, and municipal waste (landfills). Biomass can be converted into energy in several ways, like direct combustion, conversion to biogas, conversion to ethanol, conversion to methanol, and finally conversion to liquid hydrocarbons. [9] There are several developing processes for effectively using biomass for the production of hydrogen. The two major processes are anaerobic digesters and pyrolysis gasifier, the former being useful in the kW range and the later being useful at the MW range.[9] An anaerobic digester (AD) is a process that converts complex animal matter (manure) into simpler gasses (methane), this requires high nitrogen content fuels. Farmers typically use an AD to reduce their pollution in the water system. Further development of this technology could be very beneficial to the fuel cell industry. Pyrolysis gasifier are a process of thermal decomposition to produce gases (methane). This process is only efficient in large-scale production. There are also several fringe processes for creating hydrogen. One such topic, recently printed in Nature, is the use of glucose to separate hydrogen from water. Researchers reported producing 11.6 hydrogen molecules for every glucose molecule in the substrate. The researchers achieved 97% of the maximum stoichiometric yield possible, 12 hydrogen molecules for each glucose molecule. This is the highest yield of hydrogen ever obtained from glucose by a biological process.[5]

Chapter 13

PEM Fuel Cells in Automotive Applications

Fuel cell applications for vehicles have certain requirements including available space and fast power response and start up times. PEMs are currently the most widely tested and used fuel cell for non-hybrid vehicle propulsion. They are favored due to their fast start-up and response times. Though as with any fuel cell, there are difficulties in implementing them. PEMs pose the problems involved with the fuel supply. The liquid form of hydrogen has a very high energy density, yet it is expensive to produce and difficult to obtain. Storing hydrogen fuel has its own problems too, including the high combustibility of hydrogen, and hydrogen embrittlement.

Other fuel cells have been tested. DMFCs are a viable option for vehicle propulsion yet they must be developed further in order to achieve higher power densities and better stability.[10] Gasoline-supplied vehicles are undergoing research to assess their usefulness, though gasoline reforming raises problems of fuel reformation and response time.

13.1 PEM Simulation and Control

Vehicle simulations have become an important analysis tool for improving and optimizing vehicle systems. A vehicle performance simulator, VP-SIM, developed at The Ohio State University is able to simulate a variety of designs using a modular, scalable modeling approach for all power train components.[6] Recently a fuel cell system has been added to this simulation tool. The model contains a fuel cell stack and models of auxiliary components required for the fuel cell stack.

The simulation determines the efficiency of the fuel cell by a series of simple equations. The PEM fuel cell performance can be determined if the voltage, current,

and power are known to give the exergetic efficiency:

$$\epsilon_{fc} = \frac{\dot{W}_{fc}}{\dot{m}_{fc} \times LHV} \quad (13.1)$$

where \dot{W}_{fc} = fuel cell power produced [kW], \dot{m}_{fc} = mass flow rate of fuel consumed in the fuel cell reaction [kg/s], and LHV = fuel lower heating value [kJ/kg]. The fuel cell power produced, \dot{W}_{fc} , can be determined from the voltage and current:

$$\dot{W}_{fc} = \frac{V \times I}{1000} \quad (13.2)$$

where V = fuel cell voltage [V] and I = fuel cell current [A].

The simulation tool can model voltage-current density relationships, and effects of cathode pressure and fuel cell operating temperature on fuel cell voltage, power density, and exergetic efficiency can be analyzed. As shown in previous chapters the simulation showed that for a given current density increasing cathode pressure or increasing fuel cell operating temperature generally results in higher voltage, higher power density, and higher exergetic efficiency.

The simulator can scale the size of the fuel cell and determine the effects of size based on the current density.

$$I = i \times A \quad (13.3)$$

where i is the current density in A/cm^2 and A is the fuel cell active area in cm^2 . Applying this to Eq.(13.1) we obtain:

$$\epsilon_{fc} = \left(\frac{\frac{V \times i}{1000}}{(\dot{m}_{fc}/A) \times LHV} \right) \quad (13.4)$$

The use of this scaled equation allows any size fuel cell to be modeled by specifying the fuel cell active area.

As with any power generation system, a fuel cell needs auxiliary components to support the operation of the fuel cell stack. Therefore, the auxiliary components must be considered when analysing performance of a fuel cell stack in automotive applications. A schematic of a fuel cell system designed for use in an automobile is shown in Fig.13.1.

Fig.13.2 below gives the auxiliary component power per fuel cell active area equations which are all needed to successfully model the fuel cell system to determine the total efficiency. The expressions for auxiliary component power density are derived from an energy balance for each component.

With the above equations, calculations conducted by the VP-SIM include predicting the ability of a powertrain to meet a desired vehicle driving cycle, estimate fuel economy, and implement a supervisory control strategy.

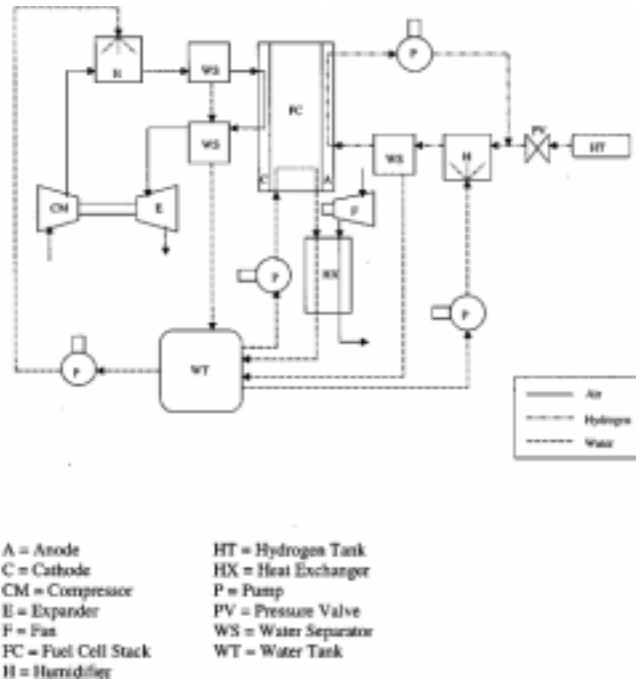


Figure 13.1: PEM fuel cell system schematic

There are other similar simulators such as National Renewable Energy Laboratory's ADVISOR or Argonne National Laboratory's PSAT.[6]

Tests have been performed using the VP-SIM by varying the fuel cell stack current density request from 0 to 0.1 A/cm^2 . The results of current density vs power density is given in Fig.13.4.[6]

The fuel economy is crucial in determining if fuel cells are more economically viable than gasoline combustion engines. Below is table giving the simulated fuel economy for various fuel cell system configurations.

13.2 PEM Cost Analysis

The cost of fuel cells are currently too high to allow them to become a economically effective alternative to current energy generation methods such as coal and gasoline burning. As with any commercially available product, the cost of fuel cells will decrease once high volume production begins.

Component	Power per Fuel Cell Active Area [kW/cm ²]
Compressor	$\dot{W}_{comp} / A = \left(\frac{\dot{m}_{air_{in}} / A \times C p_{air} \times T_{amb}}{\eta_{comp}} \right) \left(r_{p,comp} \left(\frac{k_{air}-1}{k_{air}} \right) - 1 \right)$
Expander	$\dot{W}_{exp} / A = \eta_{exp} \times \left(\left(\dot{m}_{o2_{out}} / A \times C p_{o2} \right) + \left(\dot{m}_{n2_{out}} / A \times C p_{n2} \right) \right) \times T_{cell} \left(1 - \left(\frac{P_{carb,out}}{P_{amb}} \right)^{\left(\frac{k_{air}-1}{k_{air}} \right)} \right)$
H ₂ Pump	$\dot{W}_{pumpH2} / A = \frac{\left(\dot{m}_{H2_{out}} / A \times C p_{H2} \right) + \left(\dot{m}_{H2_{out}(a)} / A \times C p_{H2(a)} \right)}{\eta_{pumpH2}} \times T_{cell} \left(r_{p,pumpH2} \left(\frac{k_{H2}-1}{k_{H2}} \right) - 1 \right)$
Air Humidification Pump	$\dot{W}_{pumpairhumid} / A = \frac{101.325 \times \dot{m}_{H2O_{airhumid}} / A \times \Delta P_{pumpairhumid}}{\rho_{H2O} \times \eta_{pumpairhumid}}$
H ₂ Humidification Pump	$\dot{W}_{pumpH2humid} / A = \frac{101.325 \times \dot{m}_{H2O_{H2humid}} / A \times \Delta P_{pumpH2humid}}{\rho_{H2O} \times \eta_{pumpH2humid}}$
Cooling Water Pump	$\dot{W}_{pumpcool} / A = \frac{101.325 \times \dot{m}_{H2O_{cool}} / A \times \Delta P_{pumpcool}}{\rho_{H2O} \times \eta_{pumpcool}}$
Cooling Fan	$\dot{W}_{fan} / A = \frac{\dot{m}_{air_{in}} / A \times C p_{air} \times T_{amb}}{\eta_{fan}} \left(r_{p,fan} \left(\frac{k_{air}-1}{k_{air}} \right) - 1 \right)$

Figure 13.2: Auxiliary component power per fuel cell active are

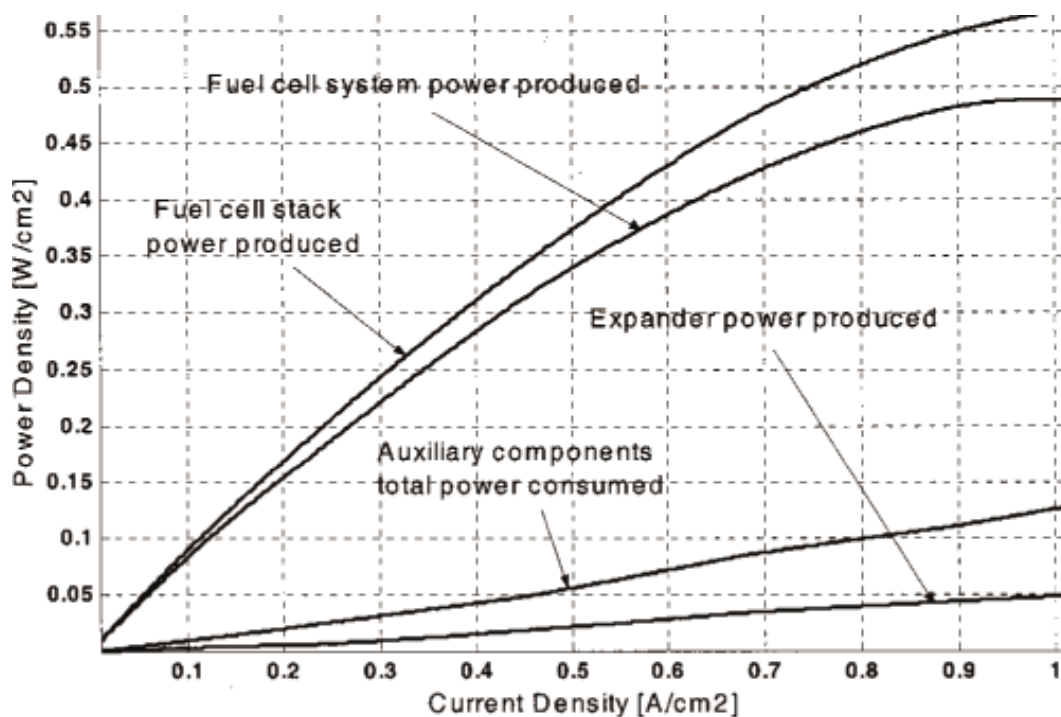


Figure 13.3: Fuel cell and fuel cell system power density versus current density given by the VP-SIM

Air Control/System Configuration Case	Fuel Economy [mpg equivalent gasoline]	Hydrogen Used [kg]
Ideal air control with expander	43.34	0.2454
Ideal air control without expander	40.85	0.2630
No air control with expander	34.48	0.3081
No air control without expander	26.81	0.3959

Figure 13.4: Warm Start FHDS fuel economies and fuel usage for various air control and system cases.

Chapter 14

Manufacturing Methods

14.1 Bipolar Plate Manufacturing

The function of a bipolar plate is to supply reactant gases to the gas diffusion electrodes via a flow field in the surface, and provide series electrical connections between the individual cells, and effectively remove product water. Bipolar Plates are a significant cost of a fuel cell therefore advances in their development is critical. Currently there are three major types being researched. These include stainless steel, titanium, and carbon/graphite composites. Manufacturing methods for bipolar plates differ depending on the material. Graphite composites are generally compression or injection molded, whereas metals are machined.

Metal bipolar plates offer a high potential to reduce costs and enhance power density versus carbon composites. For metal bipolar plates flow channels are manufactured by machining, etching or embossing. One type of metal used, stainless steels, form passive oxide surface layers which have a high ohmic resistance under PEM fuel cell operating conditions. Therefore, direct use leads to a voltage drop in the fuel cell which makes the output and efficiency too low for a commercial application. To reduce the chance of contamination and reduce contact resistance of the metallic plates various types of coatings and surface treatments have been investigated and applied to the plates. Usually oxides and nitrides (metallic based) coatings are applied by electroplating, evaporation, sputtering, and chemical vapor deposition.

The following discussion concerns stainless steel bipolar plates and their effectiveness when coated with oxides. The graph below, Fig 14.1 shows that formation of the oxide layer and nickel dissolution to the bipolar plate can be avoided by using applied coatings.[14]

The cell voltage as a function of time is shown in the graphs below. The graphs show that the coated layers are stable for at least 1000 h which is a substantial amount

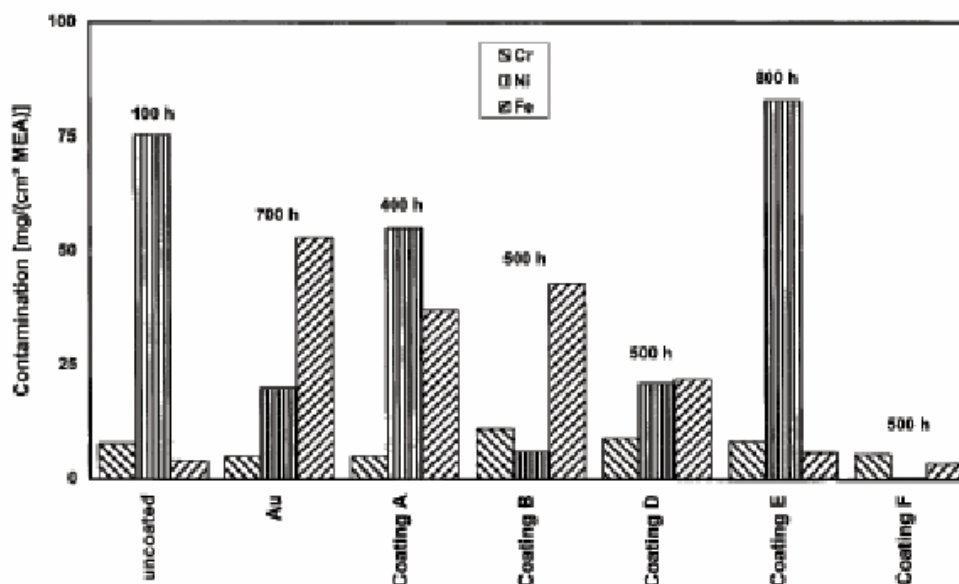


Fig. 2. Contamination of the MEA of single cells with Fe, Cr and Ni, measured after the cell test with different coated metallic bipolar plates.

Figure 14.1: Contamination of the MEA in single cells

of time for a fuel cell.

Significant ohmic losses are encountered across the bipolar plate/GDE interface which reduces the efficiency. Sample cells were tested in an endurance testing device and then the change in surface resistance was measured. Over the experimental period, there was a difference in the surface resistance between the used and the original samples as shown in Fig. 14.4.

The polarization response was shown to vary depending on the bipolar plate alloy composition which affects the performance of the fuel cell.

Fig. 14.6 shows the polarization response for the various materials.

14.2 Carbon/Carbon Composite Bipolar Plate for PEMs

High-density graphite with machined flow channels was tested. The manufacturing method was a low-cost slurry molding process to produce a carbon-fiber preform (120x140x1.5 mm).[14] The surface of the preform is sealed using a chemical vapor infiltration technique in which carbon is deposited on the surface material in sufficient

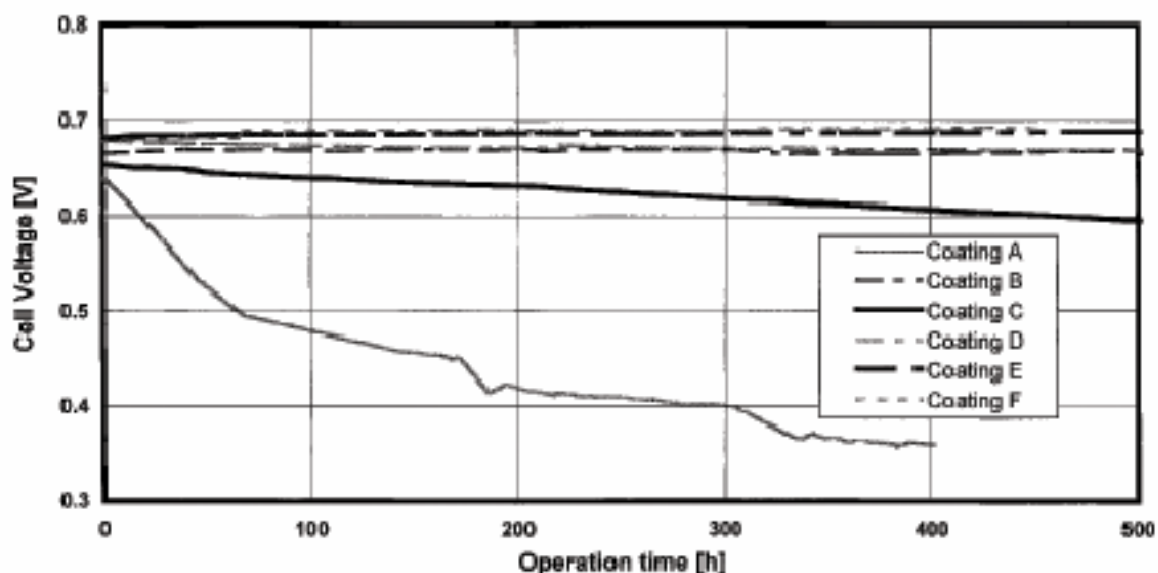


Fig. 4. Lifetime curves of single cells with bipolar plates made of stainless steel 316L coated with different coating materials.

Figure 14.2: Lifetime curve for a single cell with different coated bipolar plates

quantity to make it hermetic as shown in Fig. 14.7.

Fig. 14.8 is a picture of the bipolar plate used in the evaluation and the second picture shows a cross section of the bipolar plate with carbon deposited on it.

14.2.1 Conclusions

The proposed carbon/carbon-composite bipolar plate material has very promising fabrication, material, and performance characteristics. It is very low weight (half the weight of other materials used) which is highly beneficial. High electronic conductivity and low cell resistance which increases efficiency lends itself to continuous process fabrication and economies of scale, so costs should be greatly reduced.[12]

14.3 Electrolyte Matrix

The electrolyte retaining matrix is a porous material that gives structural integrity to the stack and contains the electrolyte. The electrolyte matrix must be wettable to an extent to provide good ionic conduction, must be free from cracks to prevent gas crossover, and must have good structural integrity.

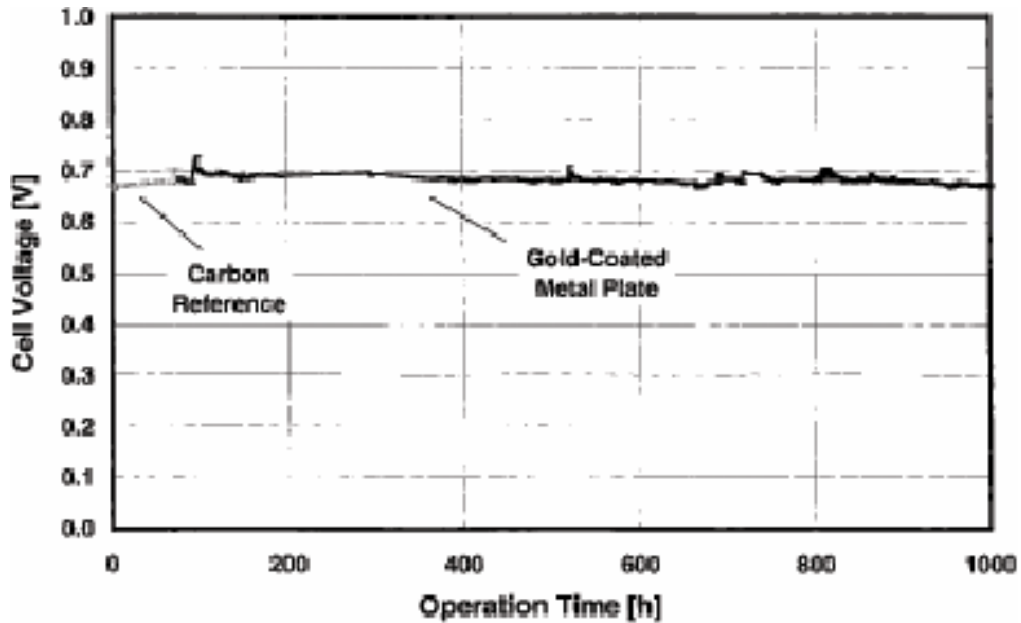


Fig. 3. Lifetime curve of a fuel cell with a gold coated metallic bipolar plate (SS316L).

Figure 14.3: Lifetime curve for a single cell with a gold coated bipolar plate

Silicon Carbide with a binder is the best matrix material for use in PAFCs Silicon Carbide slurry is prepared by the procedure below: Doctor Blade method with slurry thickness of 0.040 mm.[12] Fig. 14.11 shows the zeta potential for ball milling vs. mechanical stirring.[12] The particle-size distribution curves of as-received powder and the slurries prepared by the ball-milling and mechanical-stirring methods are shown in Fig.14.12. The particle size in the mechanical-stirred slurry exhibited tri-modal distribution with a well-separated particle-size profile. The particle size prepared with the ball-milling approaches a bi-modal type which is more advantageous.[12] Cell performance is improved with increase in milling time and reaches a maximum at 24 hrs. The matrix layer prepared by the ball-milling procedure exhibits a more uniform structure but the mechanical-stirring process produces larger pores in the matrix layer as shown by Fig.14.14.[14] Less electrolyte movement in the ball-milling matrix which results in extended cell life. [12]

14.3.1 Conclusions

Particles in slurry prepared by the ball-milling procedure exhibit high absolute zeta potential values which give good dispersion Optimum dispersion is achieved after 24

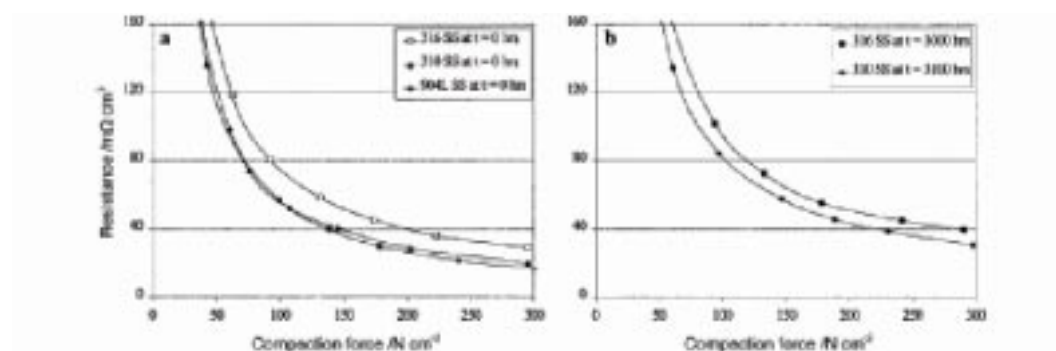


Fig. 2. Variation in interfacial resistance dependency on compaction force. (a) Before endurance testing. (b) Sometime into endurance testing. 904L cell has not yet been dismantled after 1500-h testing, thus the interfacial resistance difference could not be measured.

Figure 14.4: Resistance vs. Compaction force before and after endurance testing

hrs milling time The cell with a matrix prepared by the ball-milling method displays better performance and lifetime than with a matrix obtained by the mechanical stirring method. [12]

14.4 Introduction to SOFC and DMFC Manufacturing Methods

Although the performance parameters and the reliability are major areas of interest in making fuel cell technology more acceptable for common application, price is still the major hurdle. As has been mentioned several times in this book, the current price of fuel cells is a major limiting factor for overall market acceptance. This high price, as broken down in the SOFC chapter, has 80% of the cells cost tied to the manufacturing and production of the fuel cell. This cost is something that the industry and the government has pin-pointed as an area that is critical to reduce if the technology is ever to become a widespread reality. This cost of manufacturing and production really touches on many of the hurdles facing the fuel cell. In order to bring this price down several areas of the technology will have to be improved. Two important issues are the production and manufacturing techniques used to create the electrolyte components. To better understand the issues related to this technical hurdle, which will lead to a price reduction (the overall goal), a case study of current work on SOFC and DMFC is explained below. These cells were chosen since both are seen as the most technically possible and easiest to implement into today's current energy market.

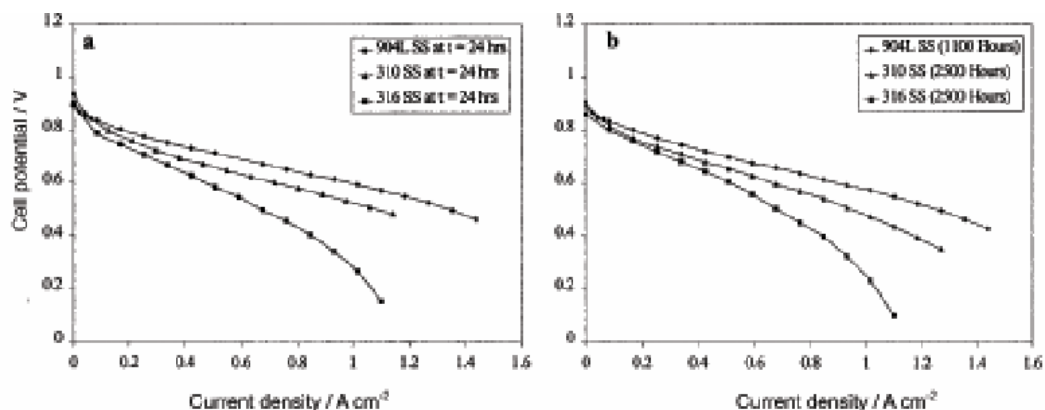


Fig. 3. Polarisation plot for each fuel cell (11.8 cm²) arrangement. Data taken at (a) after 24 h. (b) At sometime into the long-term test.

Figure 14.5: Cell Potential vs. Compaction force before and after endurance testing

14.5 Methods for DMFC

The use of a DMFC is an attractive choice due to their simplified technological hurdles. They do not require complicated humidification systems, fuel reforming, or stack cooling. They also are more adaptable to today's fuel storage infrastructure. For more specific information on the DMFC see the DMFC chapter.

An important design consideration for the DMFC is the optimization of the component thickness. The idea is to reduce the fuel cell crossover while keeping the internal resistance of the cell at its lowest possible value. This study set out to optimize this ratio while using inexpensive manufacturing techniques. Their approach was to use Nafion 112 membrane in their MEA, that would operate at STP, without additional humidification.

14.5.1 MEA Thickness and Performance

The MEAs are constructed of three parts. The first part is the structurally necessary section. This layer of .26 mm wet-proofed carbon paper was used as the backing material in this specific test. This material is necessary so there is a layer on which to build the substrate surface. This layer is also important for the connection of one cell to the next, through the bipolar plates. The middle section of the MEA is a micro porous layer. This layer serves the purpose of providing an avenue for transport of the methanol or the reacted water. The micro porous layer was formed in a two-stage process. The first stage was to create a slurry of Teflon and carbon black. This slurry was then spread across the surface in a screen-printing type of operation.

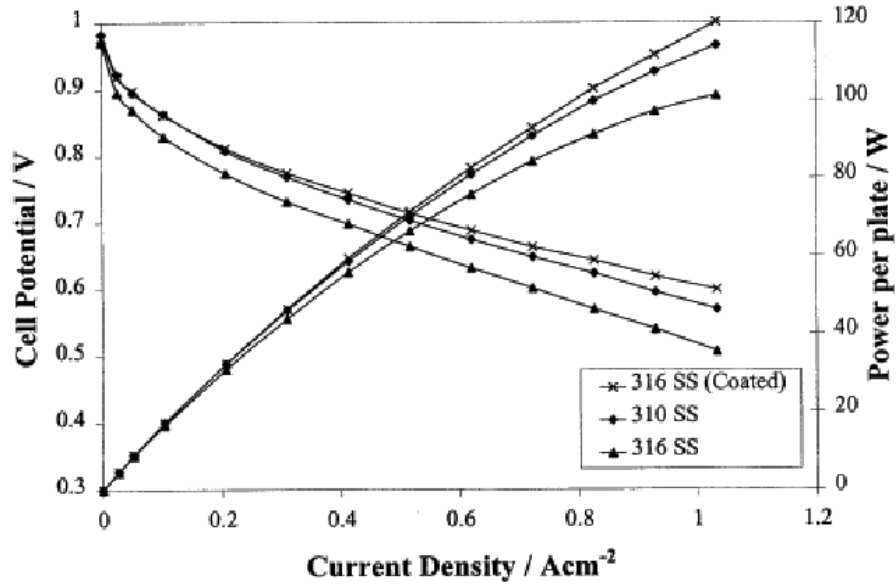


Fig. 5. 200 cm² bipolar plate comparison of 316, 310 wrt propriety coated 316.

Figure 14.6: Polarization Response for Various Materials

Once the substrate dried it was then sintered, as discussed in pervious chapters, at a temperature of $360^{\circ}C$. These two processes resulted in the layer that was $2 \frac{mg}{cm^2}$ of Teflon. The final stage was to add the catalyst layer. This layer was made from a 5 wt%. Nafion 112 solution that was formed on Pt-Ru support structure. This was manufactured using a slurry coating technique. The results of the catalyst layer are listed below in Table 14.1. Following the table is the graphical representation of the anode and cathode electrolytes, see Fig.14.15.

	Cathode	Anode
Pt-Ru	$1.3 \frac{mg}{cm^2}$	$4 \frac{mg}{cm^2}$
Nafion	$1 \frac{mg}{cm^2}$	$1 \frac{mg}{cm^2}$

Table 14.1: Loading of the Anode and Cathode in a DMFC

The goal of this new technique was to develop a thin membrane with two criterion in mind. The first was to reduce the cost of manufacturing and the second was to improve performance. The manufacturing costs were dealt with by using common manufacturing techniques. The performance of the cell was tested under several

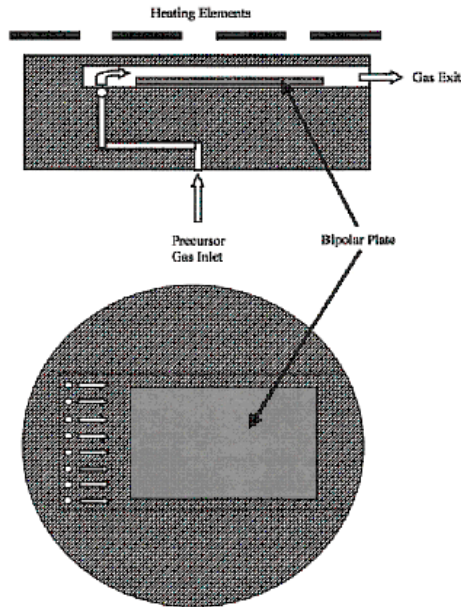


Figure 2. Top and side views of the fixture used for infiltrating the preforms showing the gas flow path.

Figure 14.7: Chemical Vapor Infiltration apparatus

conditions and the results are shown below, see Fig.14.16.

14.5.2 Effects of Compression

The next phase of the study, and an important parameter to understand in all fuel cell manufacturing techniques, is the determination of the allowable compression of the cell members. This is an important design and manufacturing characteristic. Often cells components are held together under high compressive loads for several reasons. Several of these are the importance to have small size, the necessity to keep gas leaks down, and finally to improve performance. If two materials are pressed together then they will have greater surface area contact, thus improving the number of sites for which the reaction can be performed. This study seeks to find the limit in which the cell can handle before the compressive load is no longer beneficial, or potentially even degrade performance. The following figure, Fig.14.17, shows the effect of two different compressive loads. The two compressive loads tested in this scenario were for mildly compressed and highly compressed cells. These were defined as being compressed to $\frac{1}{3}$ and $\frac{2}{3}$ of its original width for highly and mildly compressed cells, respectively. The cells that were originally manufactured were about $300 \mu m$ in thickness. The

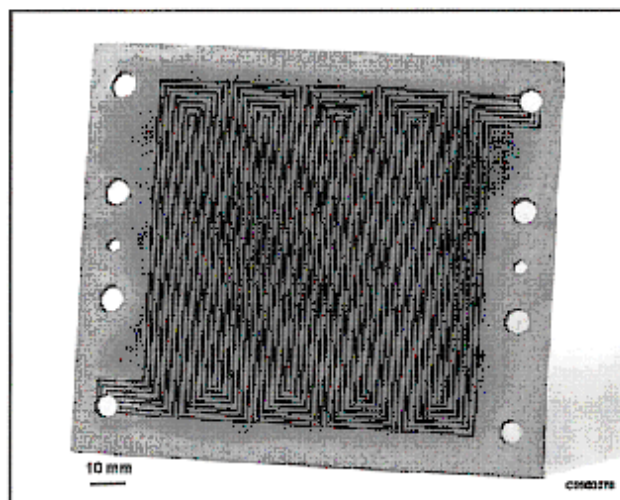


Figure 4. Prototypical Los Alamos National Laboratory design, 100 cm² active area carbon/carbon composite bipolar plate showing the flow fields and other features.

Figure 14.8: Picture of a Carbon Bipolar Plate

reason for the dramatic drop off in the voltage, see Fig. 14.17, is mainly due to the inability to support the reaction. This can be likened to a concentration loss that was discussed in Chapter 4. In that scenario the reaction rapidly dropped off in voltage because there was not enough fuel to continue to keep up with the reaction. A very similar phenomenon is also happening in this case as well. Although the system can support the flow rate of fuel, the cell cannot process the fuel, thus causing the same effect as not having the fuel. The electrolytes become damaged in the compressive loading process and only have a limited number of remaining sites for the reaction to take place on. The anode and cathode develop regions of cliffs and valleys. The regions between these two cannot support the reaction, thus dramatically limiting the usable surface area. This can be thought of in the same way one thinks about contact surfaces for purposes of friction. Although it appears to have a large contact area, the actual area of contact is dramatically less than the apparent contact area. Thus it was found that the over compression of the cells is not a beneficial technique since the cell dramatically loses performance.

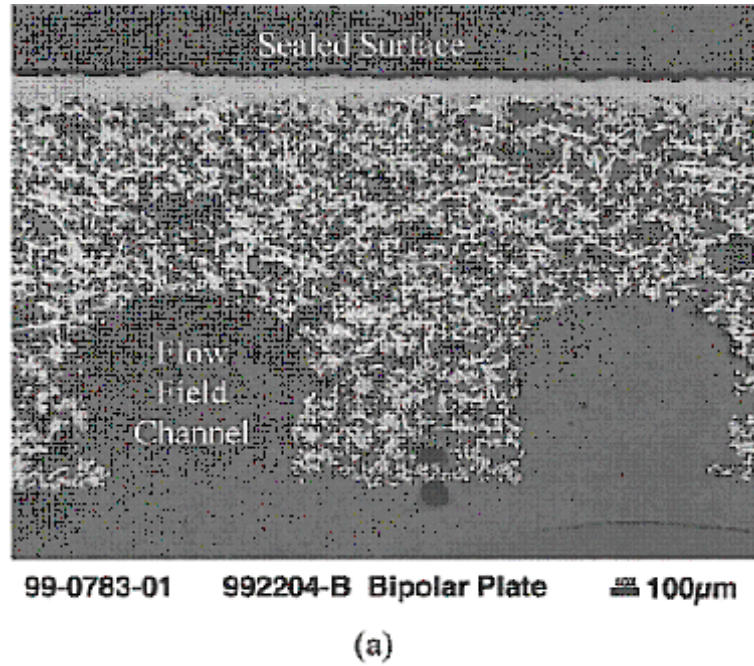


Figure 14.9: Cross Section of a Carbon Bipolar Plate

14.6 Methods for SOFC

Current solid oxide fuel cell cell-fabrication techniques require high sintering temperatures (1400°C) to obtain yttria-stabilized zirconia (YSZ) electrolytes on anode substrates. This manufacturing process causes permanent damage to the components of the cell and thus reduces the overall performance of the cell. This study has found that by reducing the sintering temperature of the YSZ it is possible to create smaller agglomerates. This results in several important cell properties. The first is improved power densities. The next is the ability to produce thinner electrolytes. The process produces $0.3 - 0.5 \mu\text{m}$ agglomerates, which produces $5 - 20 \mu\text{m}$ size electrolytes. The two following images illustrate the effects of the new manufacturing process, Fig.14.18 and Fig.14.19.

The second stage of the study was to replace the common Ni-YSZ components in a SOFC with a compound that would better be suited for the use of methanol. This was seen as an important feature, since methanol is an easy fuel to integrate into a fuel cell system. This is especially true for a vehicular system. The component chosen was $\text{Cu/CeO}_2/\text{YSZ}$. This was chosen because of its ability to directly oxidize hydrocarbon fuels. In order to manufacture the electrolytes a tape casting process

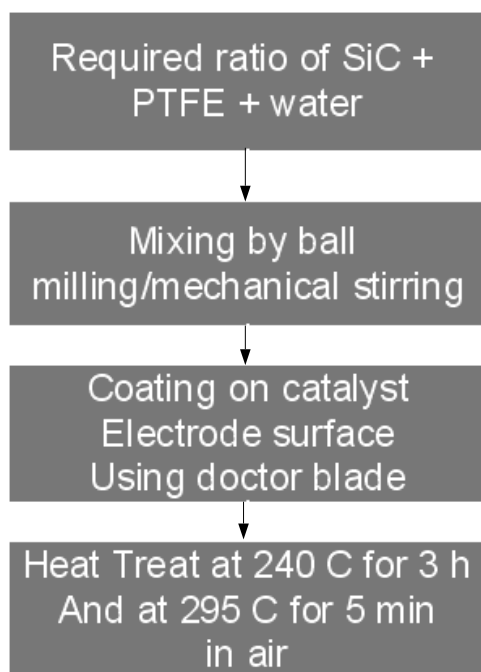


Figure 14.10: Ball Milling

was used. This is a well-understood process; it is also fairly inexpensive, thus reducing overall system costs. Fig. 14.20, shown below, illustrates this process, and how it was specifically applied to the Cu/CeO₂/YSZ membrane.

This process is not necessarily the best mass production technique, but it is a cheap, easy, and effective technology that is proven, thus allowing for the immediate production of the cells. This process would most likely be replaced by CVD, discussed earlier. This process is cheaper and quicker, thus improving the cost and time of production in a mass production setting. The following figure, Fig. 14.21, shows the results of the cell under the new sintering and Cu/CeO₂/YSZ membrane, which was developed for hydrocarbons.

This figure was produced with a liquid synthetic diesel fuel. These results would likely be better if the gaseous methane were used instead.

14.7 Conclusion

The work of a wide variety of groups, along with the work by the preceding two groups, is helping to improve the characteristics of the fuel cell. They are seeking to decrease

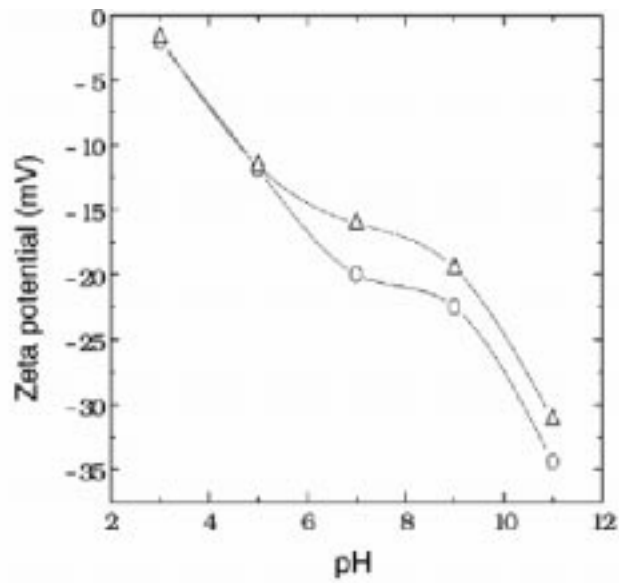


Fig. 2. Effect of pH on zeta potential of SiC particles in slurry prepared by (○) ball-milling, and (Δ) mechanical-stirring methods.

Figure 14.11: Zeta Potential

the system cost, while improving the performance. Once these two parameters can be realized fuel cell systems will come to dominate the energy conversion market.

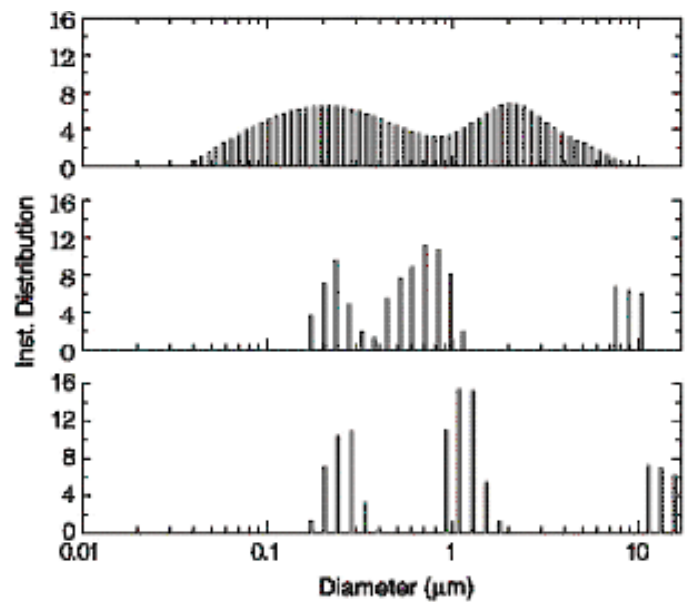


Fig. 4. Particle-size distribution of as-received SiC powder (top), and ball-milled (middle), and mechanical-stirred (bottom) SiC slurries.

Figure 14.12: Particle Size Distribution

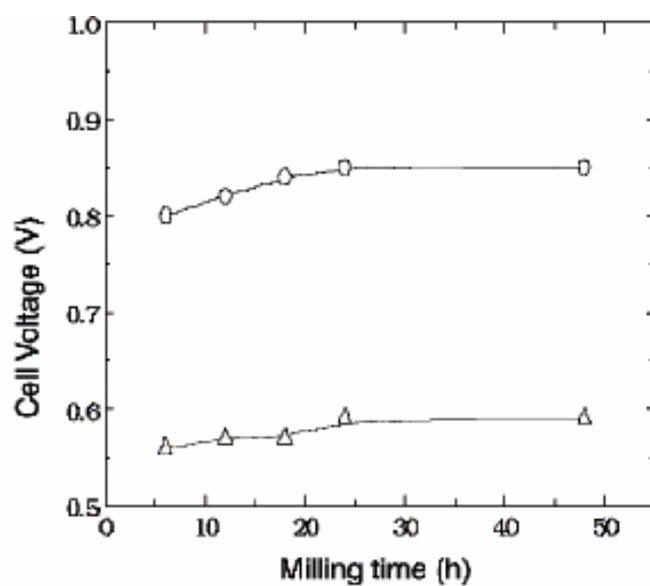


Fig. 5. Effect of ball-milling time of SiC slurry on open-circuit voltage (○), and on cell voltage (△) at constant current density of 100 mA cm^{-2} .

Figure 14.13: Milling Time

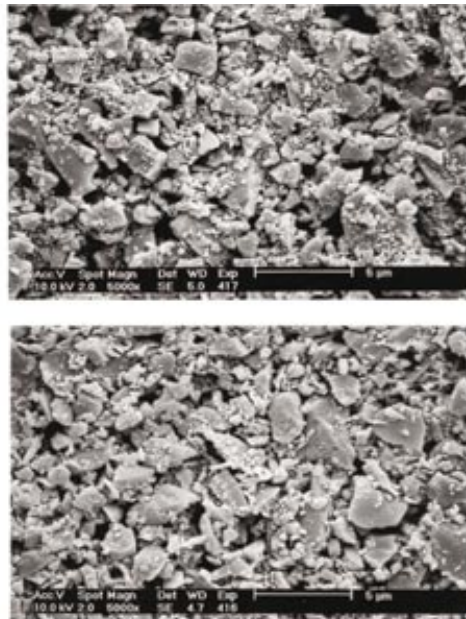
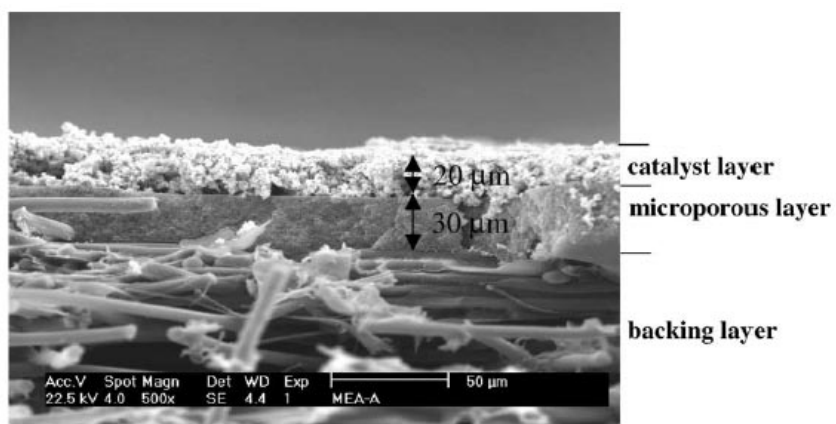
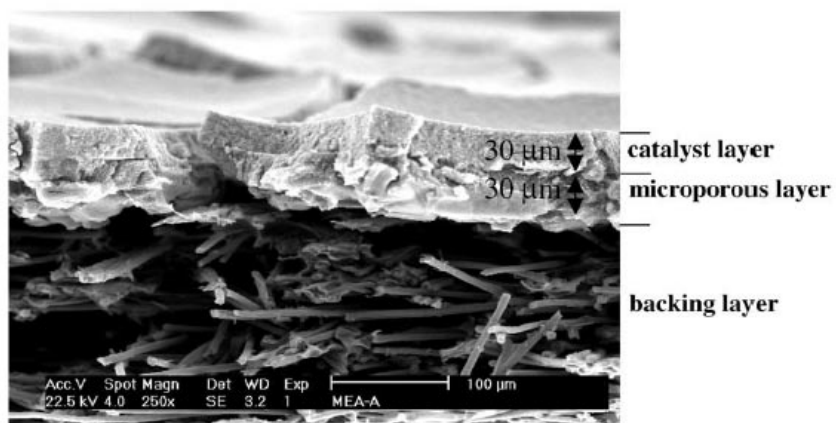


Fig. 8. Surface structure of SiC layer prepared by mechanical-stirring (top), and ball-milling (bottom) methods.

Figure 14.14: SEM of particle size for the machine milling(top) and ball milling(bottom)



(a)



(b)

Figure 14.15: The MEA for the anode (a) and the cathode (b)

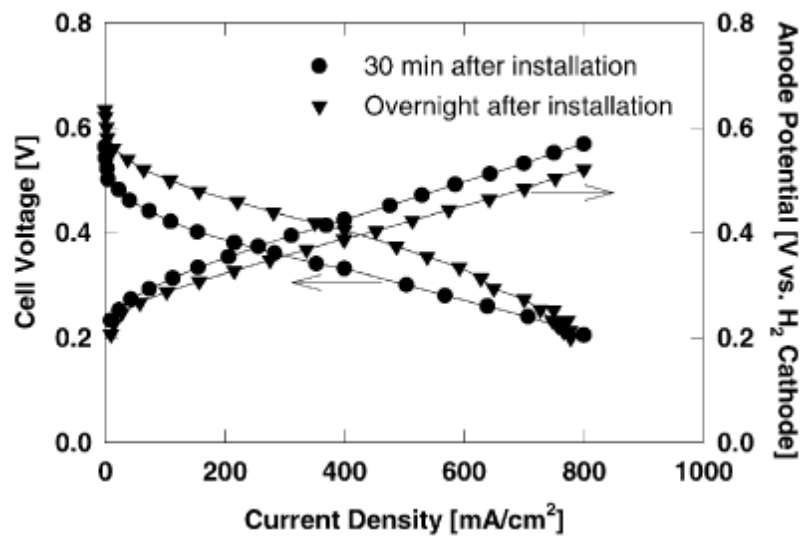


Figure 14.16: Cell Performance, given the new membrane

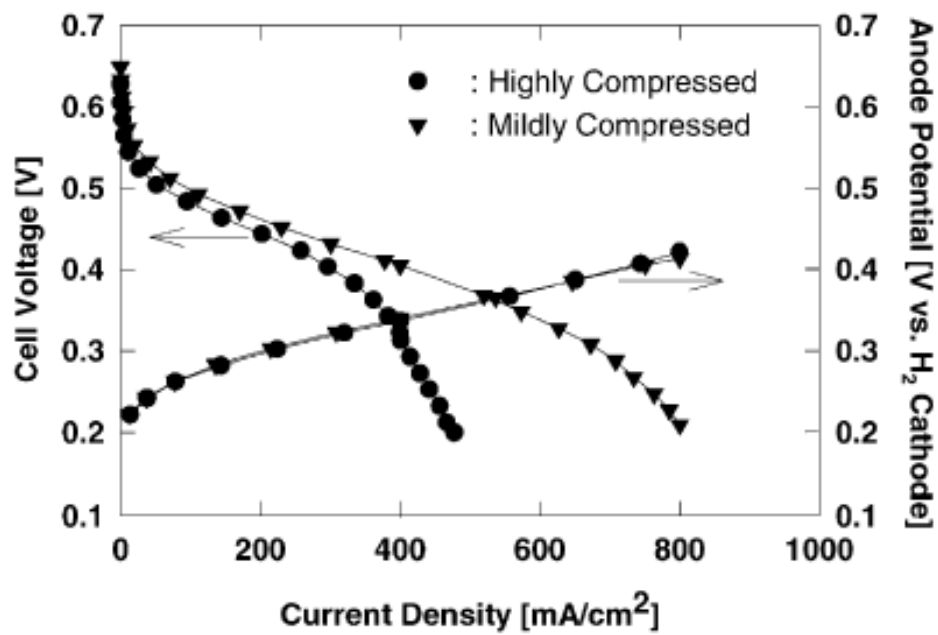


Figure 14.17: Effects of Pressure on the Cell

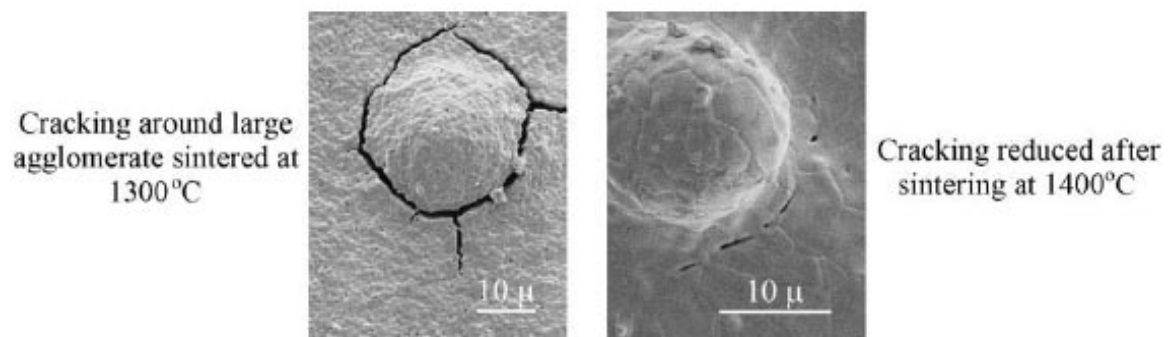


Figure 14.18: Cracking of the agglomerates at lower temperatures

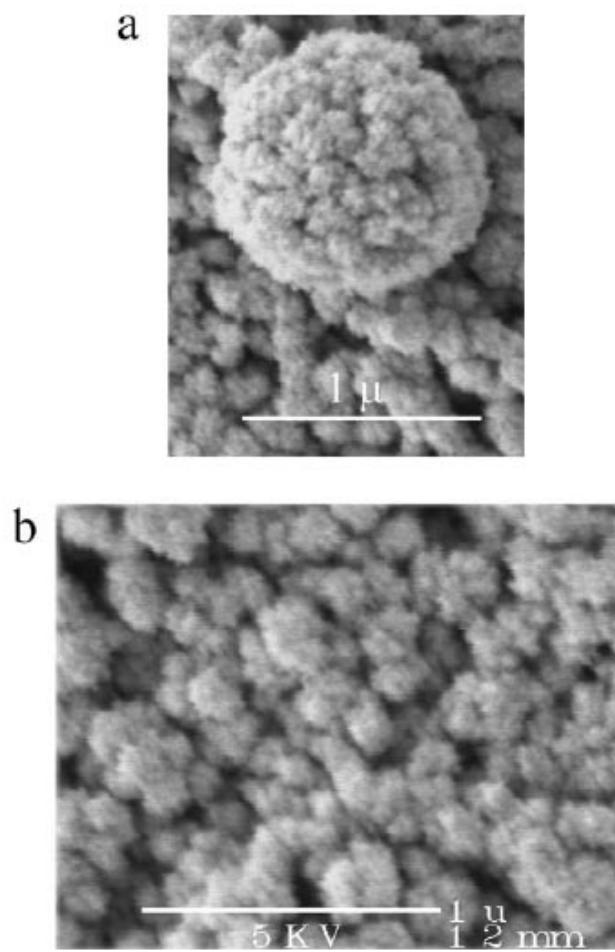


Figure 14.19: The reduction in size of larger agglomerates

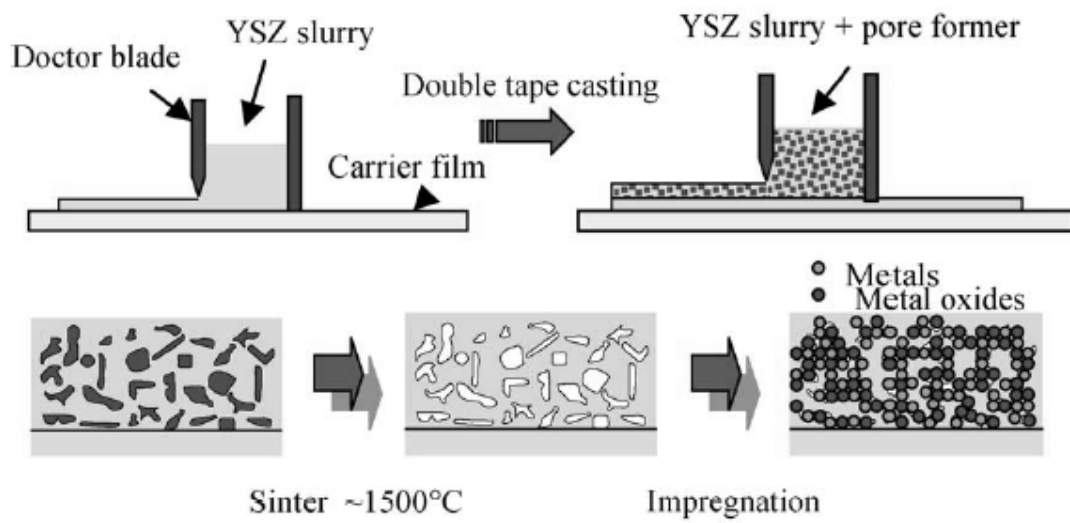


Figure 14.20: Tape Casting of SOFC

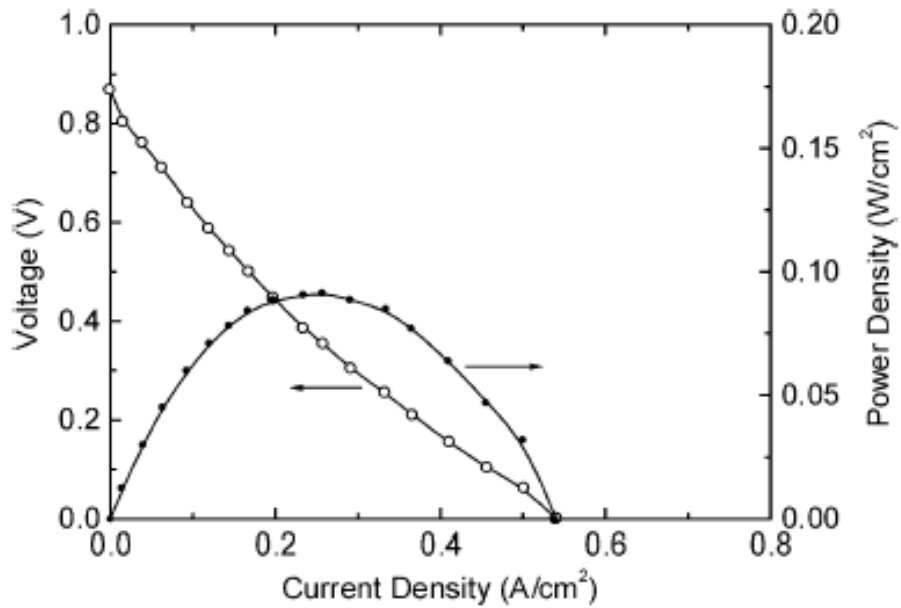


Figure 14.21: Performance of the SOFC using the new manufacturing and design techniques

Chapter 15

Portable Fuel Cells

15.1 Introduction

As technology advances and our dependence on portable electronics increases, so does the demand for powering these devices. To accommodate this growth we must improve our ability to power portable consumer electronics. The functionality, operating speed, and lifetime of portable devices are often constrained by the available power supply. Fuel cells are able to provide this need for increased power. Fuel cells potentially offer 5-10 times greater energy densities than rechargeable batteries.

15.2 Solutions

Research is currently being pursued to create microreactors with two main approaches: (1) using silicon processing technology to create an integrated structure, and (2) miniaturizing the individual components, e.g. miniaturized heat transfer manifolds, and assembling them into a reactor.[11]

The first approach is being pursued by a group at the Massachusetts Institute of Technology, from which has come many excellent examples or demonstrations. They have developed a partial oxidation reactor as seen in Fig. 15.1.

Advantages of the integrated approach are the ability to control thin-film properties and their interfaces, enabling optimized reactor performance. Another advantage is that process sensors and control logic can also be built into the same substrate, facilitating on-board closed-loop control.

The other form of research for microreactors, miniaturizing the individual components, has been pursued by many groups including the Institut für Mikrotechnik, of Mainz, Germany (IMM).[11] This approach is advantageous when materials used in silicon processing are not compatible with the reaction. Another advantage is that its

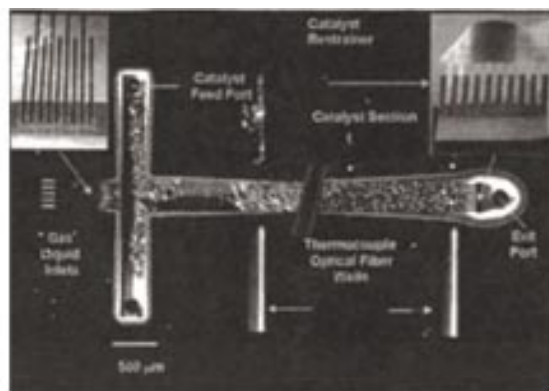


FIG. 3. Integrated microreactor showing inlet ports, exit port, fluid bed reactor, thermocouples, optical fibers, and catalyst retaining structures (see Ref. 45).

Figure 15.1: Integrated microreactor showing inlet ports, exit port, fluid bed reactor, thermocouples, optical fibers, and catalyst retaining structures

possible to integrate sensors, such as thermocouples, into the miniaturized elements even though this is not common practice.

15.2.1 Silicon Based Microreactor

Two alternative designs to the silicon based microreactor are examined in the following discussion. One involves a bipolar design using separate Si wafers for the anode and cathode that are sandwiched together, and the second is a monolithic design integrating the anode and cathode onto a single Si surface. The bipolar design is shown in Fig. 15.2.[11] The process by which the bipolar fuel cell design is manufactured is shown in Fig. 15.3. The alternative design is the monolithic design, shown in Fig. 15.4.[11]

The monolithic design is unlike the previous design in that it is coplanar and not stacked together. The anode and cathode are on the same substrate. The advantage of this approach is the ability to form all of the components on the same structure, analogous to IC or MEMs manufacturing.[11] This design also allows the humidification control of the membrane to be separated from other control circuits, e.g., reactant flow and temperature stability. The coplanar structure does reduce the produced power density by 50% which is a significant amount when comparing this power density to that of batteries. Another problem is that the current must now be pulled out by the metal lines, requiring them to be relatively large to minimize ohmic impedance.[11]

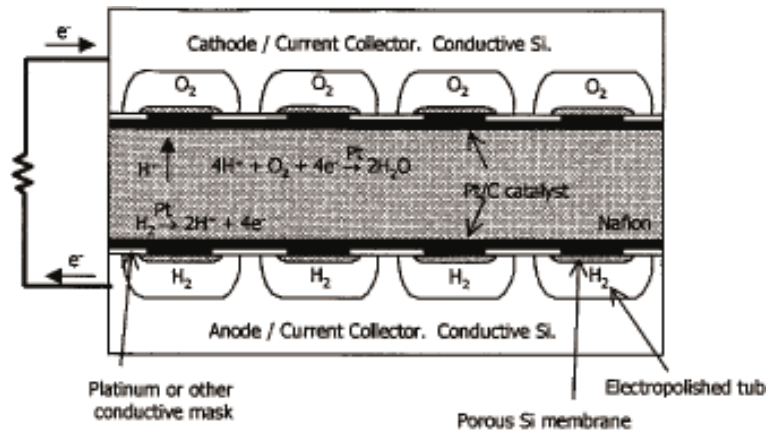


FIG. 4. Cross-sectional schematic of bipolar fuel cell design.

Figure 15.2: Cross-sectional schematic of bipolar fuel cell design

15.3 System Issues

A portable power system must be capable of delivering reliable well regulated voltage while being able to respond quickly to the fluctuating power demand. In order to successfully design a portable fuel cell for electronic devices, the whole system must be taken into consideration. [11]

15.3.1 Thermal Management

The formation and dissipation of heat in small electronic devices such as laptop computers is a major concern and limiting aspect of the power supply. The majority of energy consumed by portable electronic devices is released as heat. Therefore, it is difficult to manage the thermal load within portable devices. Some electronic devices use fans to carry away heat, while other devices, which operate at peak power for short periods of time, use materials with high specific heat to absorb the excess heat. Including such materials does not reduce the maximum steady-state temperature, but it extends the time that the device stays relatively cool. [11]

Fuel cells though, make this problem of thermal management even worse. Oxygen reduction has very poor kinetics; therefore, a H_2/O_2 fuel cell operating near its maximum power density is only 50% efficient. This means that for every 1 W of electrical energy produced, the fuel cell will create 1 W of heat.[11] Therefore, a device rated for 1 W must transfer a total of 2W. This is shown in Fig. 15.5

As can be seen from the figure, the heat efficiency of a methanol/ O_2 fuel cell is

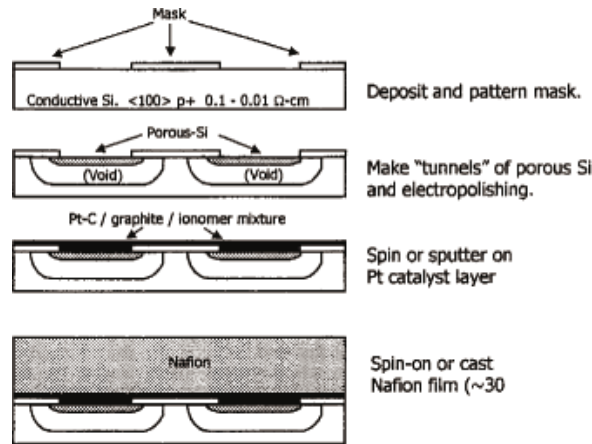


FIG. 5. Process flow to form one side of the bipolar device.

Figure 15.3: Process flow to form one side of the bipolar device

greater than that of the H_2/O_2 fuel cell. For every 1 W of electricity generated by a methanol fuel cell, approximately 2W waste heat is generated requiring total thermal dissipation of 3 W.[11]

15.3.2 Air Movement

The issue of gas transport to the anode and cathode is an important topic for portable fuel cells. The transport of oxygen to the cathode is very important to ensure the fuel cell continues to function. The easiest way to obtain the oxygen is through the air. This also requires that only the fuel needs to be stored with the device.[11]

The easiest way to achieve air contact with the cathode is expose the entire surface of the cathode to the open air environment. This solution provides excess oxygen to the cathode, and during short time use, the excess oxygen will remain which is beneficial. Longer durations of use will decrease the available oxygen if no air convection is present which increases the path length for oxygen diffusion and decreases the power output of the fuel cell. Fig. 15.6 shows a schematic depiction of a possibility for the required cathode area needed on a laptop computer to ensure adequate oxygen supply.[11]

Fig. 15.6 is the required surface area for a laptop computer operating at peak power of 20 W. Some comparisons of different types of fuel are interesting to note. A cell operating on H_2 , requires approximately 31 cm^2 to create 20 W, but a lower efficiency methanol fuel cell increases the required area to approximately 133 cm^2 if operated at the most favorable conditions for methanol, 4.8 bar air and 80°C .

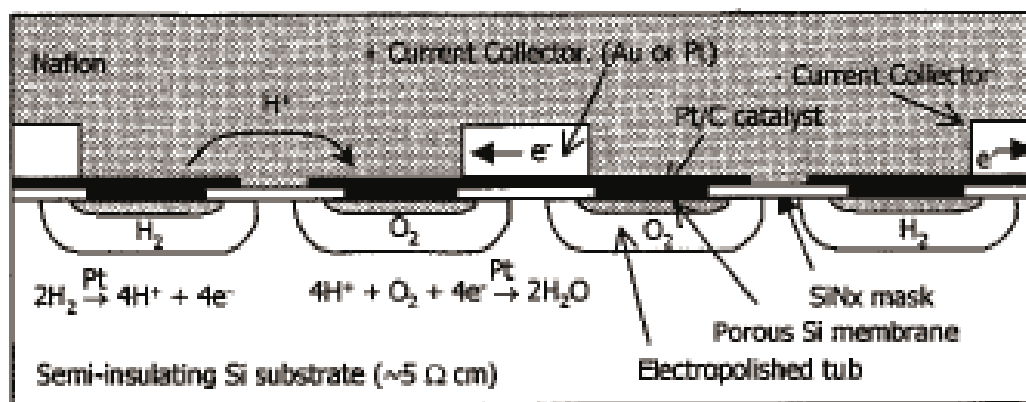


FIG. 9. Cross-sectional schematic of monolithic fuel cell design.

Figure 15.4: Cross-sectional schematic of monolithic fuel cell design

If the same methanol fuel cell is operated at 70°C and at atmospheric pressure, the required area increases to 400 cm^2 , basically the whole surface area of a typical laptop computer.

15.3.3 Fuel Delivery and Crossover Prevention

In order for a portable fuel cell device to compete with battery powered devices, it must contain both the fuel cell and the means of fuel storage and delivery. Without the choice of a fuel reformer, which adds considerable complexity and cost, there are two options for portable fuel. The two options are hydrogen and methanol. Liquid methanol has greater volumetric energy densities than hydrogen, therefore is a more suitable fuel for portable devices. The higher energy density allows longer operating times between refueling. The disadvantage with using methanol is the increased cell stack size because the kinetics of methanol oxidation are worse than hydrogen.

Another problem with the use of methanol arises because of the boiling point of methanol, 65°C which is in the range of a normally operated fuel cell, $60 - 100^{\circ}\text{C}$. Therefore, a slight back pressure must be applied on the anode to prevent the feed stream from boiling.[11]

Methanol crossover is another issue to be aware of when using methanol as the fuel. Two main approaches to solve address this issue involves: (1) the regulation of the methanol feed concentration, or (2) inserting a barrier layer within the fuel cell. The first approach works by simply maintaining a feed concentration just above the minimum necessary to provide methanol to the anode which will considerably

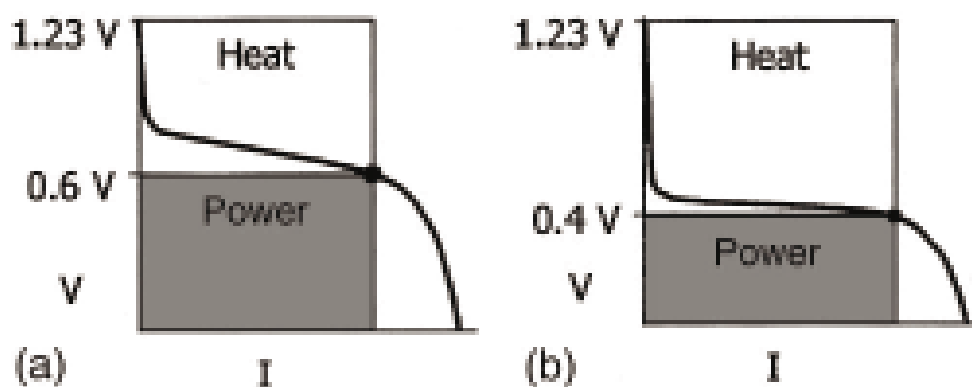


Figure 15.5: Schematic polarization curves for (a) H_2/O_2 and (b) methanol/ O_2 fuel cells

reduce the crossover rate. This approach is advantageous if the load profile is either constant or known before application. Therefore, power spikes are not handled well with this approach. The feedback monitoring device is also complicated and costly. The second approach uses a barrier generally permeable to hydrogen, but it rejects methanol. The disadvantage comes from an additional interface and the inherent increase in resistance. The increased resistance decreases the power that can be delivered per unit cross-sectional area.

15.3.4 Load Management

The ability for the system to react to different load requirements is crucial to the effectiveness of portable fuel cells in electronic devices. As a result of the speed at which electronic devices operate, a fuel cell must be able to respond very quickly to changes in the load, and they have to be capable of doing this from a cold start. Since a fuel cell operates at its peak performance at an ideal operating temperature, there is a transient that results as the fuel cell takes time to reach this operating temperature. This becomes a problem in extreme cold environments, and decreases performance considerably. The fuel cell also had reduced performance from a dry start before the membrane has become sufficiently hydrated.[11] This can take several seconds for the water produced at the cathode to diffuse across the membrane and provide it with sufficient hydration to produce power at peak levels. Solutions to these problems, are to either make the fuel cell larger so that it can supply the required power at start up, or add an auxiliary power supply for the start up requirements.

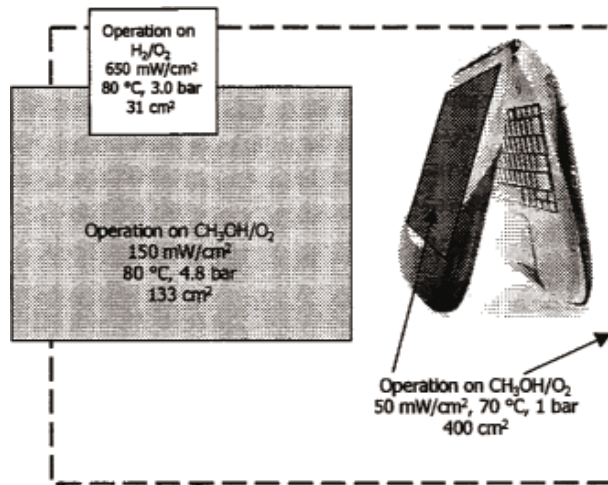


Figure 15.6: Relying on passive air supply requires large area of fuel cell to be exposed to air. This problem can be mitigated by active air supply but at the cost of higher complexity and cost

15.3.5 System Integration

By leveraging silicon manufacturing technology, it is hoped that a complete solution that includes the fuel cell, the fuel and oxidant distribution network, and the monitoring and control electronics can be developed. The system must take fuel and air as inputs and reject water and heat, and the protocol for handling these inputs and outputs must be carefully considered.[11]

Chapter 16

The New fuel for a New fleet of Cars

16.1 Introduction

If fuel cell vehicles are to have any significant long-term impact in the auto industry automakers, and suppliers, must successfully address commercialization challenges that loom over the auto fuel cell industry, stated a recent report by Roland-Berger Strategy Consultants. [4] The report identified the most difficult among the challenges as low-cost infrastructure, range, and power density. Other challenges include cost reduction, component integration and, complexity and safety issues. [4] One of the more important features that the study found was the necessity to have uniformity and standardization of how the vehicles of the future will be fueled. The topic of fueling the fuel cell is so important because it is the fuel itself that has motivated much of the recent drive to develop hydrogen fuel cell technology. Gasoline, the most common fuel in use now, is not environmentally friendly, and is a potential security risk for a nation without vast sources of gasoline. Since the fuel cell operates on hydrogen is seen as a cleaner fuel, and one that everyone has access to, hydrogen is the most abundant element in the world. The question that needs to be answered by proponents of fuel cell technology will be how to get and efficiently use this new fuel, and all at a lower cost than gasoline. As mentioned previously there are several compelling advantages to a hydrogen economy, but according to a DOE study [13], unless hydrogen is comparable in cost to current technologies, it will not gain vast market acceptance. The study found that despite the other benefits of a hydrogen economy, price is the only driving factor in the success or failure of the technology.

To use pure hydrogen in a fuel cell it must be produced, or reformed, from other compounds or processes. These differences in production process and origin of

hydrogen are what needs to be standardized by the industry before auto fuel cells become commercially possible.

16.2 Fuel Reforming

16.2.1 Gasoline Reforming

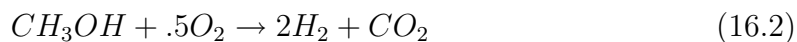
Since the infrastructure of a gasoline driven vehicle fleet already exists, it seems logical that gasoline would be one of the more popular choices for providing a source of hydrogen. The reforming of gasoline (C_8H_{18}), however, is not pollution free and the weight to hydrogen ratio is lower than other potential options. Gasoline also still forces the dependence on a nonrenewable fossil fuel, which is not evenly dispersed through the world. Since there is already an infrastructure setup for delivering and storing gasoline on board vehicles it is only necessary to overcome the problems of reforming the fuel for acceptable use in a fuel cell. The reforming of gasoline must be run at an elevated temperature ($1100 - 1500^\circ C$), thus part of the gasoline is oxidized (burnt), and then the full catalytic oxidation occurs, which is run at temperatures of $800 - 1000^\circ C$. In order to achieve high efficiencies of fuel conversion a nickel catalyst is used to promote full reforming of the gas. The POX, partial catalytic oxidation, and full catalytic zones are separated to ensure that a pure stream of gas flows to the reformer. If only pure gasoline is present then Eq.(16.1) describes the reforming process.



Since gasoline often contains a variety of impurities a CO and sulfur reformer are necessary. (These detoxification processes are described in an earlier section). This reforming process can either be done on-board or remotely. If the process is remote then the storage of pure hydrogen will be needed onboard, see next section for details on hydrogen storage.

16.2.2 Methanol Reforming

Methanol is seen as another viable source for hydrogen production. Since methanol produces less CO it is seen as a possible better choice for fueling fuel cells, especially when it can be produced from renewable sources. The partial oxidization of methanol results in the following equation.



The necessity for cleanup on a methanol system is less stringent than a gasoline reformer. Often the presence of CO is converted into CO_2 , by using some of the produced hydrogen, also the removal of sulfur is rarely a problem, since sources of methanol do not contain high a content of sulfur.

The following figure, Fig. 16.1, shows the differences between the auto thermal reforming process and the steam reforming process described earlier.

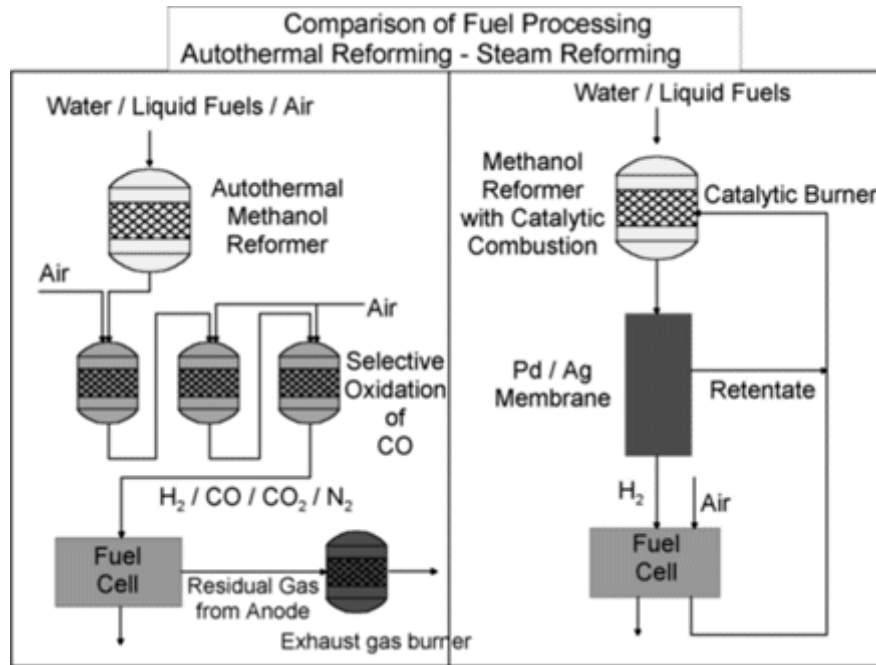


Figure 16.1: Comparison in fuel reforming processes

16.3 Fuel Storage

16.3.1 Compressed Gas

This process is simple and easy approach to hydrogen storage. The technical problems are widely understood and thus the process is mostly optimized. Since this is a developed technology it is most likely not a good choice for the long-range outlook on the storage of hydrogen. Although the process is possible it is not very efficient, and as mentioned above, cannot be greatly improved upon. In this scenario the gas is typically held in containers at pressures near 200 bar, some can go even higher (1200

bar is the burst pressure in one tank) [7]. Since hydrogen has such a low density it is very difficult to hold it, even under these high pressure. In a typical steel cylinder at 200 *bar* only .036 *kg* of hydrogen is stored per 3.0 *kg* of tank mass. To ensure that the tank does not leak hydrogen, hydrogen is very small and thus can escape through the lattice of some metals, it is necessary to choose an appropriate material. This material also must be resistant to hydrogen embrittlement. This occurs when the hydrogen finds its way into internal blisters and then promotes crack propagation. The storage of hydrogen in tanks is possible in the automotive industry, and is currently being used in a 15 bus fleet that is being deployed throughout the EU. Several tanks will be placed on the roof of the busses and will then be fed to fuel cells in the rear of the bus. This process is a relatively simple process that is well understood, thus making it a valid choice as a stepping stone application of hydrogen storage.

16.3.2 Cryogenic Liquid

Another stepping stone technology for the storage of hydrogen is the cryogenic freezing of the gas and converting it into a liquid state. This is a costly operation, since it must be not only pressurized, but also held at 22 *K*. It is still a convenient, and currently the only possible way to store large amounts of hydrogen. Although it is the most efficient way to store larger quantities of hydrogen it has also been explored by a several German companies for its possible use in cars, a small-scale operation. BMW has developed a hydrogen internal combustion engine that uses liquid hydrogen. The liquid hydrogen is stored onboard in a 50 *kg* container. It stores 120 *L* (8.5 *kg*) of LH_2 . In this system the hydrogen must be preheated, usually by a heat exchanger, before it is fed into the fuel cell.[4] This is because the liquid fuel is not possible in a fuel cell. The applicability of this process is also demonstrated by BMW. They operate several company cars on liquid hydrogen stations, thus proving that is possible to build an infrastructure on LH_2 . There are several safety issues that need to be considered with the use of liquid hydrogen. The first is the possibility of severe frostbite. Since the liquid is super cooled at 22 *K* any contact with bare skin will cause the skin to tear and freeze.[4] Also this low temperature means that it is necessary to insulate all surfaces to prevent the liquid from boiling. This insulation is also necessary since liquid air, which can form if the LH_2 comes into contact with the air, is very combustible.

16.4 Conclusion

Although there are other technologies for the storage of hydrogen, such as metal hydrides and nanotubes, they are not seen as possible uses in the near term. The metal hydrides are simply too heavy and the nanotube technology is too new and

some evidence even suggests that it is faulty. The reforming of gas or methanol is a valid option for fuelling vehicles, but it will add system weight and complexity. Although technology may be able to make the system light enough to be onboard, it is possible that users would rather have shorter ranges on the cars and pay less, then have the opposite. The other option is have onboard reforming of fuels since it will be easier to adapt our current infrastructure to handle a liquid based fuel source. The following image, Fig. 16.2, is an artists representation of how an on-board fuel cell reforming car may be designed.

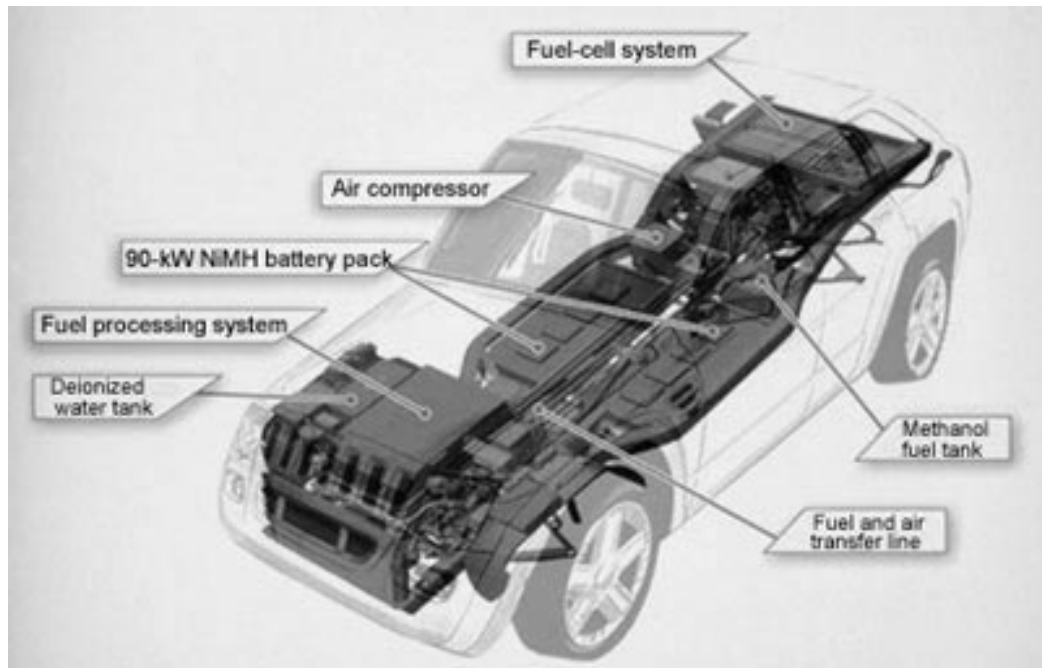


Figure 16.2: FCV: Methanol Reforming On-board

Chapter 17

Commercial and Industrial Use

17.1 Introduction

Stationary power is one of the most mature applications for fuel cells. Stationary fuel cell units are used for backup power, power for remote locations, stand-alone power plants for towns and cities, distributed generation for buildings, and co-generation. These FC systems can either be used to supplement grid power, or be used as supplemental units. It is possible to only have the fuel cell active during peak times, thus reducing the total cost of energy. Second auxiliary uses for fuel cells are in the area of backup. If there is a need for backup or redundant power a distributed energy solution is needed, and the fuel cell is a very efficient form of reliable backup. It is estimated that more than a thousand of the smaller stationary fuel cells (less than 10 kilowatts) have been built to power homes and provide backup power. [13] Polymer electrolyte membrane (PEM) fuel cells fueled with natural gas or hydrogen is the primary design used for these smaller systems. This move from centralized power to distributed power is an area that will continue to see growth and development in the next century. Until recently, economies of scale were orienting the power production systems towards large centralized units located away from the urban areas. But when using independent energy conversion units (FC systems) to provide the various energy forms required by an urban infrastructure, such as heating, cooling and power, a considerable amount of primary energy is wasted into the atmosphere. Thus the efficiency of a system increases when all by-products of the fuel cell system can be used effectively. The following figure shows the performance of a typical SOFC stack, see Fig. 17.1.

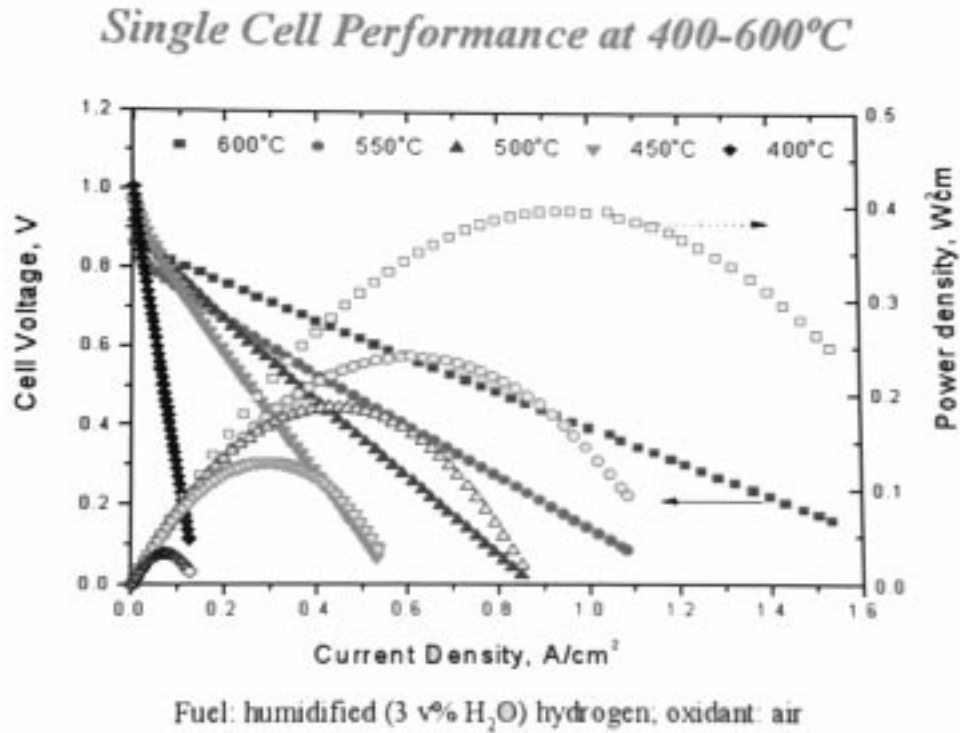


Figure 17.1: Overall Performance Of Individual Cell

17.2 Optimization of a Cogeneration Plant

The simulation of the plant considers a superstructure including a solid oxide fuel cell-gas turbine (FC-GT) combined cycle, a compression heat pump, a compression chiller and/or an absorption chiller and an additional gas boiler. This system will try to optimize all components and thus provide an overall efficiency and an overall power cost. These two issues will be the determining factors in evaluating if the system is a viable system for commercial use. A thermo-economic optimization of the design and operation of a district heating, cooling and power generation unit composed of an FC-GT combined cycle, associated with a heat pump, a compression chiller and/or an absorption chiller, and an additional gas boiler has been undertaken with regards to cost and CO₂ emissions.[4]

17.2.1 Thermodynamics

The optimal fuel cell in this arrangement is the SOFC, since it has a very high overall efficiency and it produces a high quality exhaust heat. This heat will be used to increase the system efficiency even higher. Solid oxide fuel cells (SOFCs) can provide highly effective energy conversion systems, when their high temperature exhaust gases are expanded within a gas turbine. Efficiency can then be increased up to 70% with an appropriate integration into a CHP system.

The following diagram, Fig. 17.2, shows the thermodynamic cycle used in this case study. This system employs SOFC's and a gas turbine. As mentioned above,

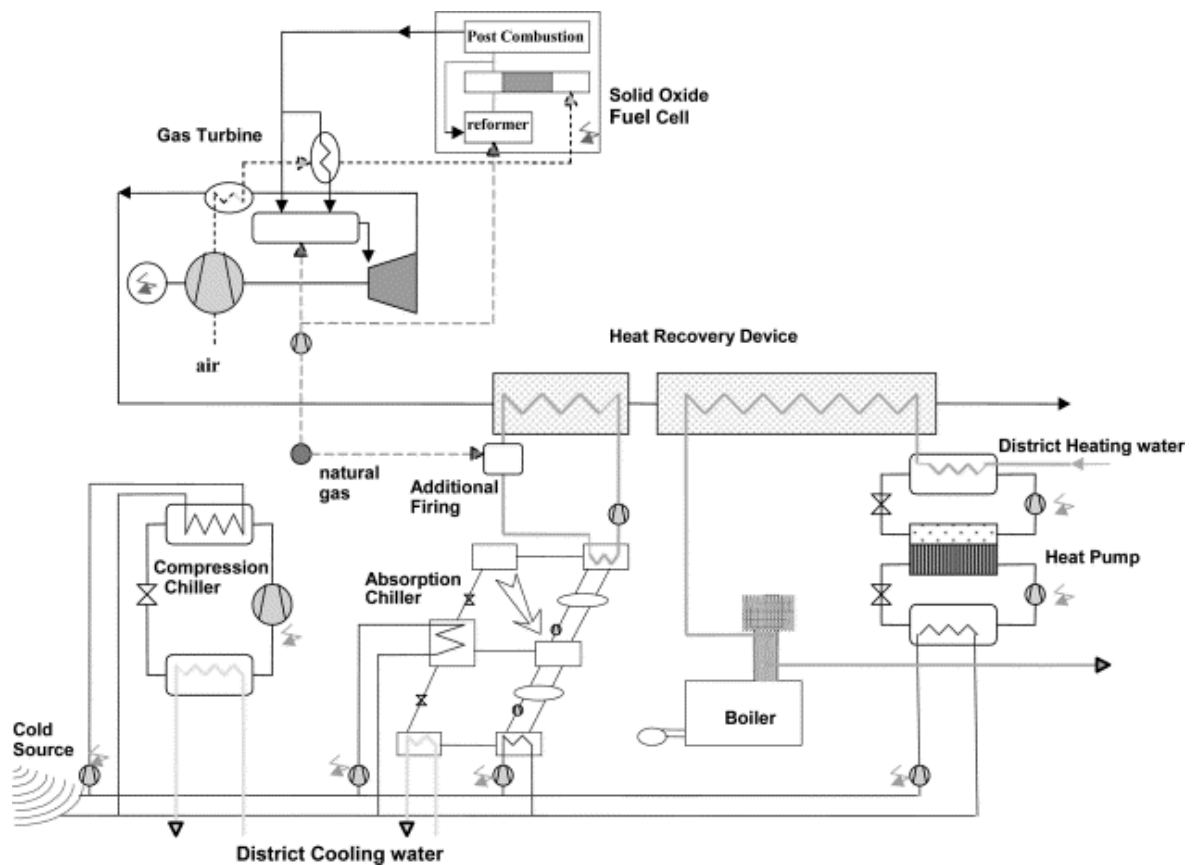


Figure 17.2: Thermodynamic Cycle of entire FC system.

this combination will increase the overall efficiency of the system to close to 70%. The other components of interest are the AC-DC inverter, a transformer, pre-heating

heat exchangers, piping, insulation materials, a combustion GT, air/fuel compressors, a generator, and sub-assemblies such as the control panel, the reduction gear, inlet-outlet ports, and piping for the GT system [4]. As shown in Fig. 17.2, the return line of the district heating first enters the condenser of the compression heat pump. This choice is obvious since the coefficient of performance (COP) of the heat pump will benefit from the low temperature difference between a cold source at a fairly stable temperature (local body of water) and the return temperature from the users. Since the temperature of the network can be adapted to the season, the COP of the heat pump should reach its highest value in summer when the temperature corresponds only to domestic hot water requirements. The water is then driven to the heat recovery exchanger of the combined cycle in order to recover part of the remaining heat in the exhaust gases of the gas turbine. Finally, the water is driven to the additional boiler that upgrades the temperature of the water to the temperature level of the supply line. If part of the cooling load remains uncovered by the absorption unit, an additional compression chiller is introduced. After pre-heating the air, the exhaust gases of the GT are driven to a last heat recovery device in order to recover part of the remaining heat for use in the district heating water or in the absorption chiller's de-absorber loop. In any environment, the water exiting the heat recovery device is imposed to be in liquid state. The amount of heat recovered is derived from the knowledge of the water and gas enthalpies at the entrance of the heat exchanger [4].

The following graphic illustrates the dependence of the system on pressure, see Fig. 17.3. This graph, like the ones displayed in chapters two and three, illustrate

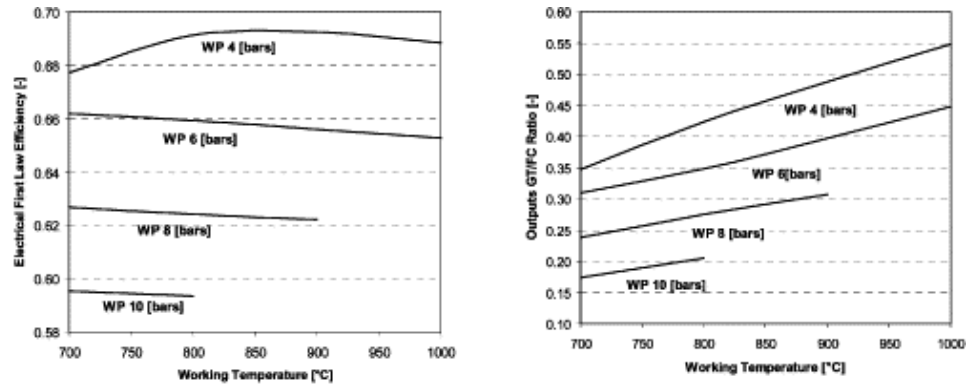


Figure 17.3: Electrical efficiency of the FC-GT cycle (left) and ratio between electric power generated GT/FC (right)

the high dependence of the operating pressure on the system. These effects are also

felt by the components of the system, besides the fuel cell. The increased cost, to benefit ratio of supercharging the system was not considered in this analysis. This will have to be completed in a more through analysis.

17.2.2 Cost Analysis

The cost analysis for this system is a very important result of this study. If the system is efficient, but not cost effective it is not a reasonable system to implement. Also the amount of toxins, in the form CO_2 is another critical issue. Since this system will operate in a congested environment it must have extremely low emissions. The following figure shows five configurations and their results. The following figure shows

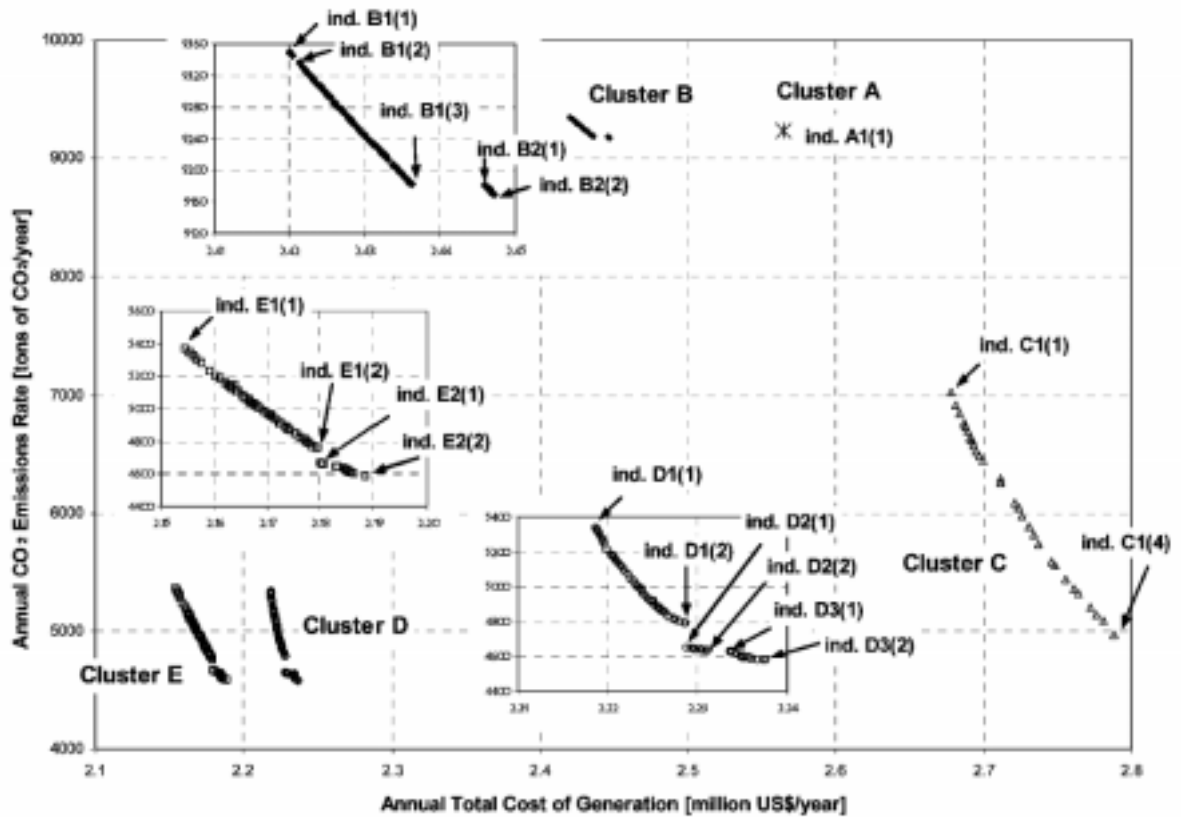


Figure 17.4: Cluster Options

some of the possible configurations, and their costs, see Fig. 17.5. Cluster A, and its

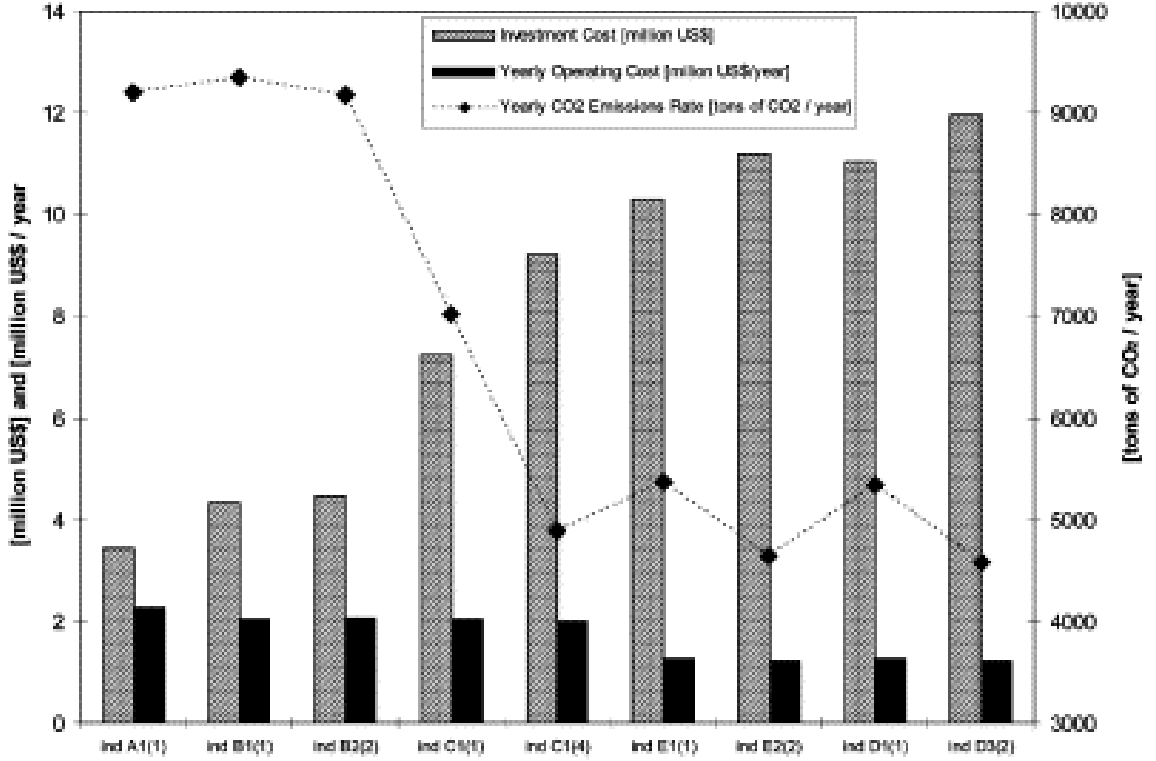


Figure 17.5: Cost Analysis for several configurations

single individual A1(1), can be seen as a reference since all the heating load is covered by a natural gas boiler and all the cooling load by a compression chiller, with the totality of the required power imported from the grid [4]. This option is the one that requires the lowest initial investment, with about \$3.4 million, but also that induces the highest yearly operating cost of about US \$2.3 million. The yearly emissions rate is of 9200 tons of CO₂ per year.[4]

A jump into the cluster B corresponds to the introduction of a small capacity (500-700 kW) FC-GT combined cycle as a co-generation unit. It induces an increase of the investment cost by about 25%, but reduces the yearly operating cost by about 10%. This is explained by: (1) a much higher efficiency in summer of the FC system; and (2) a high price of electricity in summer (which is avoided by the FC). Note that the efficiency and emissions in winter remain the same since the FC-GT is shut down during this period. Higher emission rates than the reference case are explained by the fact that although the CO₂ emission rate per unit of power produced is very low compared to other thermal power units, due to a high electrical efficiency, it remains

of the same order than the one of the grid mix since part of the grid power is non-fossil based . [4]

If a heat pump is introduced instead of the FC-GT unit (cluster C), the CO₂ emissions rate can be significantly reduced, up to 47% lower with a 170% higher investment cost (case of individual C1(4) with a 8 MW heat pump). Although the operating cost is reduced, thanks to a high global efficiency, the total annual cost is much higher due to a much larger investment cost. [4]

An option, which at the same time reduces the annual total cost and the annual emission rate is obtained with the association of a heat pump and a FC-GT unit. Cluster D corresponds to such a choice with the introduction of a simple-effect absorption chiller. [4]

Cluster E with a compression chiller uses the option of an absorption chiller and is not recommended here. Since power exportation is not allowed, the electricity produced has to be used for driving a compression chiller, and thus induces the investment in two different chillers rather than a single one of larger capacity. As a result, the solution with a single compression chiller drives to a lower total annual cost. The FC-GT is designed for the midseason power internal requirements with a power outputs from 1.18 to 1.22 MW. Operating temperature and pressure remain the same along the curve with 700C and 4 bars, respectively. The electric efficiency of the FC-GT is 67.7% with a corresponding specific investment cost of 1,615.00 \$/kW. [4]

17.3 Conclusion

This cost analysis illustrates the fundamental principles that would accompany the design process necessary before implementing a co-generation plant. Although these systems are still more expensive than a traditional system, they are technically feasible, and within the range of current technology; in some cases vastly superior to current technology. Clusters D and E provide an excellent avenue for reducing the creation of CO₂, a cut of CO₂ emissions by half compared to current business as usual. When high electricity and natural gas prices are encountered, these advanced integrated energy systems represent a promising option in the near future, both economically and environmentally. Other fundamental advances will soon follow these advances in the system, such as increased power density and decreased size of the fuel cell. Once advances are made, and the price of the system falls, co-generation plants will not only become an economically viable option; they will become the best option for implementation.

Chapter 18

Fuel Cell Challenges

Fuel cells have a lot of problems that must be solved before economical implementation into society can be achieved. Among these challenges include cost reductions, reliability, and system integration. Cost reductions are vital to make fuel cells comparable in cost to other methods of energy formation. The reliability of fuel cells must be great enough as to extend the life of the fuel cells to the same as other energy means. Finally, the system integration must be capable of gaining the public's interest by showing real examples of fuel cells in use and the results of such implementation.

18.1 Cost Reductions

Cost reductions are vital to the success of fuel cells because the public will not accept and use technology that is not economically advantageous. For example, until fuel cells can decrease the price per kW, the public will continue to use internal combustion engines to power automobiles.

The high capital cost of fuel cells is the most important limiting factor in the widespread implementation of fuel cells in society. Both capital and installed cost (the cost per kilowatt required to purchase and install a power system) must be reduced in order for fuel cells to compete with contemporary energy generation methods. In the stationary power market, fuel cells could become competitive if they reach an installed cost of \$1,500 or less per kilowatt. Currently, the cost is in the \$4,000+ range per kilowatt. In the automobile sector, a competitive cost is on the order of \$60 - \$100 per kilowatt, a much more stringent criterion. [3]

Due to the high capital cost on a dollar per kW basis, significant resources have been put toward reducing the costs associated with fuel cells. Specific areas in which cost reductions are being investigated include [3]:

- Material reduction and exploration of lower-cost material alternatives

- Reducing the complexity of an integrated system
- Minimizing temperature constraints (which add complexity and cost to the system)
- Streamlining manufacturing processes
- Increasing power density (footprint reduction)
- Scaling up production to gain the benefit of economies of scale (volume) through increased market penetration.

The fuel cell cost migration path is shown in Fig. 18.1.[3]

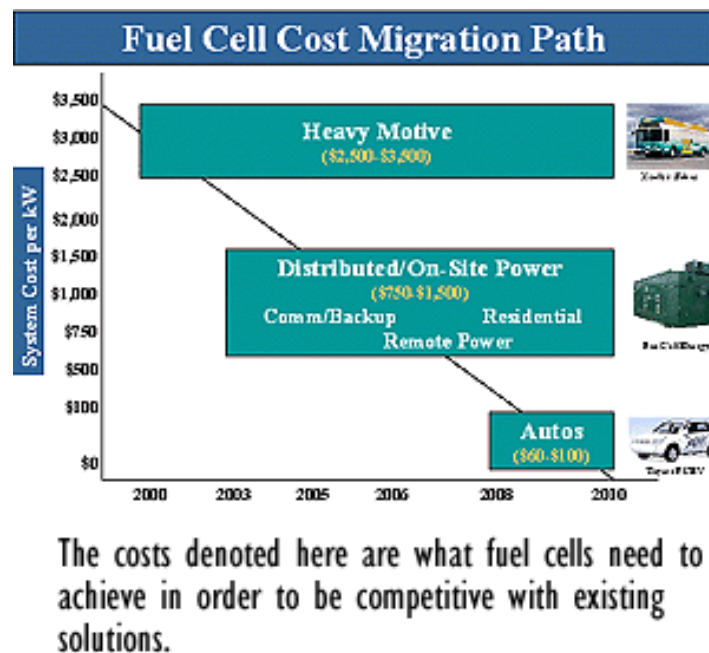


Figure 18.1: Fuel cell cost migration path over the next 10 years

18.2 System Integration

Two key systems integration issues for the success of fuel cells are: (1) the development and demonstration of integrated systems in grid connected and transportation

applications and (2) development and demonstration of hybrid systems for achieving very high efficiencies.

Integrated fuel cell systems must be developed and demonstrated in order to minimize the cost of electricity. For most applications, this requires that the fundamental processes be integrated into an efficient plant when capital costs are kept as low as possible. Specific systems and system integration R&D that is occurring today includes: (1) power inverters, (2) power conditioners, (3) hybrid system designs, (4) hybrid system integration and testing, (5) operation and maintenance issues, and (6) robust controls for integrated systems.[3]

Fuel Cells have been integrated into many parts of society to test the various results. One such integration is M-C Powers molten carbonate fuel cell power plant shown in Fig. 18.2. "M-C Power Corporation has tested a commercial scale power generator in San Diego, California, using molten carbonate fuel cells, the next generation of fuel cell technology.[1] The San Diego test unit, installed at Marine Corps Air Station Miramar, consisted of a fully integrated system including a newly designed reformer and a stack with 250 cells each with an 11 ft^2 active area. The unit reached 210 kW capacity and cogenerated up to 350 lbs/hr of steam used for heating buildings on the air station. Total output was 158 megawatt-hours of electricity and 346,000 lbs of steam over 2350 hrs of operation. In the current program, the Miramar facility is being modified to conduct performance verification testing of advanced stack designs and other improvements prior to building prototype units for commercial demonstrations at several sites by early 2001.[1]

The world's first hydrogen and electricity co-production facility opened in Las Vegas, Nevada, in November 2002.[2] The facility (built by Air Products and Chemicals, Inc., in partnership with Plug Power Inc., the U.S. Department of Energy, and the City of Las Vegas) will serve as a "learning" demonstration of hydrogen as a safe and clean energy alternative for vehicle refueling. The facility includes small-scale, on-site hydrogen production technologies, a hydrogen/compressed natural gas blend refueling facility, and a 50 kW PEM fuel cell system that supplies electricity to the grid. The fueling station and power plant are located at the existing City of Las Vegas Fleet & Transportation Western Service Center. Other partners include NRG Technologies in Reno, Nevada, who is retrofitting the 6 buses donated by the City of Las Vegas that will be refueled at this station, and the University of Las Vegas, who is modifying a bus to burn hydrogen in an internal combustion engine and to store the hydrogen in a compressed tank. A hydrogen fuel cell produced at this facility is shown in Fig. 18.3.[2]

The Sunline Services group hosts what has been called the world's most complex hydrogen demonstration project to date in California's Coachella Valley. [2] Buses running on hydrogen and hydrogen/natural gas mixtures are used for public transport and filled at Sunline's public access fueling island. Two different types of electrolyz-



Figure 18.2: M-C Power's molten carbonate fuel cell power plant in San Diego, California, 1997

ers, one supplied by a photovoltaic grid and the other by a natural gas reformer, produce hydrogen on-site. A full training program, including a curriculum for the local community college, has been developed. More than 5,000 visitors a year from around the world have toured Sunline's facilities. Sunline's experience and leadership is instrumental in establishing a knowledge base and developing codes and standards for hydrogen production and use. This is shown in Fig. 18.4. [2]

Underground mining is a promising commercial application for fuel cell powered vehicles. Conventional underground traction power technologies cannot economically meet the increasingly strict mining regulations regarding safety and health of mine workers. In this application, a fuel cell powered underground vehicle offers lower recurring costs, reduced ventilation costs, and higher productivity than conventional technologies. Proton exchange membrane fuel cell stacks, coupled with reversible metal hydride storage, a four-ton locomotive has undergone safety risk assessment and preliminary performance evaluations at a surface rail site in Reno, Nevada. The project is a collaboration between Vehicle Projects LLC, the Fuelcell Propulsion Institute, and Sandia National Laboratories. [2]

One possible commercial application for several-hundred watt fuel cells is in pow-



Figure 18.3: A hydrogen fuel cell produced at the first hydrogen

ering personal mobility vehicles, such as wheelchairs and three-wheeled electric powered "scooters" often used by the elderly or infirm. The users of these types of vehicles are often located in environments, such as nursing homes and hospitals, where hydrogen supply could easily be established. A Victory personal mobility vehicle, a scooter, manufactured by Pride Mobility Products Corp. (Exeter, PA), was modified to accept a midrange fuel cell system built by researchers at Los Alamos National Laboratory. An onboard electronics package protects the fuel cell and stores information that can be used to optimize the operation of the fuel cell. The scooter is operational and will be compared to a conventionally equipped scooter of the same model. [2]

One of the tasks of the California Fuel Cell Partnership is to evaluate fuel cell-powered electric buses in "real world" applications. Up to 20 buses using hydrogen fuel will be placed on the road beginning in 2004 for a two-year demonstration. Two fuel cell suppliers, International UTC Fuel Cells and Ballard Power Systems, will develop the transit bus engines. Three transit agencies have joined as Associate Partners AC Transit (in the San Francisco Bay Area), SunLine Transit Agency (in the Palm Springs area), and Santa Clara Valley Transportation Authority (in the South Bay Area) to serve as initial test sites for the Bus Program. The California Fuel Cell Partnership is also evaluating fuel cells in light-duty vehicles, looking at a variety of feedstock fuels for the hydrogen required for the fuel cells. [2]



Figure 18.4: Sunlines demonstration of a hydrogen refueling center.

18.2.1 Reliability

Fuel cells have the potential to be a source of premium power if demonstrated to have superior reliability, power quality. They must also be shown capable of providing power for long continuous periods of time. Fuel cells can provide high-quality power which could be a very advantageous marketing factor for certain applications. The power quality along with increased reliability could greatly advance the implementation of fuel cell technology.

Although fuel cells have been shown to be able to provide electricity at high efficiencies and with exceptional environmental sensitivity, the long-term performance and reliability of certain fuel cell systems has not been significantly demonstrated to the market. Research, development and demonstration of fuel cell systems that will enhance the endurance and reliability of fuel cells are currently underway. The specific R&D issues in this category include: (1) endurance and longevity, (2) thermal cycling capability, (3) durability in installed environment (seismic, transportation effects, etc.), and (4) grid connection performance. [3]

18.3 Technical Issues

18.3.1 Fuel

The two major issues concerning the fuel for the fuel cell revolution are the storage of hydrogen and the availability of hydrogen. The fuel cell requires pure hydrogen



Figure 18.5: An underground mine locomotive

in order to drive its reaction, and the ability to provide this hydrogen is critical. The two options for providing hydrogen are the storage of pure hydrogen or the on-board reforming of hydrogen. Both issues have advantages and serious technical hurdles. The second issue for fueling the fuel cell is the ability to get hydrogen, or some hydrogen rich fuel, to the fuel cell. This means the development of a hydrogen infrastructure. This would cost millions of dollars and a huge commitment by the government and industry. Both issues must be solved before the fuel cell can achieve wide spread market acceptance.

The first option for the fuel cell is to use an onboard hydrogen storage technique. It is currently difficult to store enough hydrogen onboard a FCV to allow it to travel as far as a conventional vehicle on a full tank of fuel. Fuel cells are more energy-efficient than internal combustion engines in terms of the amount of energy used per weight of fuel and the amount of fuel used vs. the amount wasted. However, hydrogen gas is very diffuse, and only a small amount (in terms of weight) can be stored in onboard fuel tanks of a reasonable size. This can be overcome by increasing the pressure under which the hydrogen is stored or through the development of chemical or metal hydride storage options. Researchers are developing high-pressure tanks and hydride systems that will store hydrogen more effectively and safely. The second option is to have a system for onboard reforming of hydrogen. This system adds weight and complexity to a design. Thus makes it more difficult to implement in small handheld devices, especially due to size requirements. This issue is being addressed by trying to develop micro fuel cells and micro fuel cell reformers. This technique will integrate the fuel cell system and will use the knowledge and techniques of microprocessor technology.



Figure 18.6: A mobile vehicle for handicapped people powered by a fuel cell

The second area of potential cell reforming will occur in the FCV project. This will be necessary if the storage of pure H_2 becomes difficult or expensive. This will most likely be used, in the FCV project, since methane has a higher energy density than pure H_2 . This reforming process will add to the system weight, complexity, and size; but it will provide the user with a longer range of operation and it will relieve many of the new safety issues that will be necessary if pure H_2 is used in FCV's.

The other major hurdle for the industry and the government will be how to get hydrogen to the consumers. The extensive system used to deliver gasoline from refineries to local filling stations cannot be used for transporting and storing pure hydrogen. New facilities and systems will be required to get hydrogen to consumers, this will take significant time and money. This major shift in energy policy will be necessary if the benefits of a hydrogen society can truly be appreciated. The current problems that are being faced in this area are not technically dominated. Although technical advances are always a benefit to a problem the short-term issue are those of policy, money, and time. Since the production of H_2 is already possible on a large scale it is only a matter of developing the infrastructure to produce and deliver the fuel to consumers.

18.3.2 Technological Developments

Fuel cells need to experience a few breakthroughs in technological development to become competitive with other advanced power generation technologies. These technological breakthroughs will likely occur directly through support of innovative con-



Figure 18.7: A refueling station designed for the California Fuel Cell Partnership

cepts by national labs, universities, or in industry. These innovative concepts must be well grounded in science, but can differ from the traditional fuel cell RD&D in that they investigate the balance of plant, controls, materials, and other aspects of fuel cell technology that have not been previously investigated. Innovative and fruitful concepts might be found in these areas:

- New fuel cell types
- Contaminant tolerance (CO, sulfur)
- New fuel cell materials (electrolyte, catalyst, anode and cathode)
- New balance of plant (BOP) concepts (reformers, gas clean-up, water handling, etc.).

In order to accomplish these goals the government has taken steps to improve the technological state of the industry. The government has initiated modeling to simulate the kinetics of oxidation of hydrogen and other constituents of the anode exhaust gas and the formation of pollutant species at the catalytic spent gas burner. With an inlet temperature of 323 K (50°C), the oxidation of H proceeds slowly, but with increasing inlet temperatures, the oxidation of H proceeds much more rapidly (at 350 K). This modeling activity will be validated using experimental data and used to minimize emissions of regulated and unregulated trace pollutants. Future modeling will be conducted to examine the oxidation of other species including methane and other hydrocarbons. Conventional low-temperature, copper-zinc oxide catalysts for

the water-gas shift reaction must initially be activated by reducing the copper oxide to elemental copper. This reaction is exothermic and must proceed under carefully controlled conditions to avoid sintering of the catalyst. Once activated, the catalyst must be protected from exposure to ambient air to prevent re-oxidation and must operate at less than 250°C to avoid degradation of the catalyst's activity. Conventional high temperature iron-chromium catalysts also require activation through pre-reduction and lose activity upon exposure to air. Rugged, thermally stable, shift catalysts with equal or better kinetics are needed that do not require activation nor lose activity upon exposure to air, as well as catalyst supports with high surface areas. In the longer term, the program is targeting higher-risk development of high-temperature, inexpensive membranes, and oxygen catalysts. Typically, fuel cell stack operating temperatures are limited to 80°C. Key advantages would be obtained from the development of an inexpensive, high-temperature membrane operating at 100-150°C that sustains current densities comparable to today's membranes and does not require significant humidification. This membrane would enhance CO tolerance and reduce heat rejection permitting a dramatic reduction in the size of the condenser and radiator. As mentioned earlier, higher operating voltages are required to meet efficiency targets for fuel cell systems. The development of improved oxygen reduction electro catalysts with enhanced kinetics would be beneficial because the most significant contributor to cell voltage loss is polarization. Additionally, advanced oxygen catalysts could reduce or eliminate the need for air compressors, used for supercharging, in fuel cell systems.

18.3.3 Government Interaction

The government is very dedicated to the use of hydrogen as a fuel for the American public. Although it feels that a completely hydrogen based economy will begin with a hydrogen based fleet of vehicles. The government, for several reasons, has targeted this area as a first step in developing the technology. The first reason is that the auto industry has deep pockets, thus they will be able to financially help in the conversion to a hydrogen economy. Second the range of many military vehicles could be greatly enhanced by the benefits of a hydrogen economy. Third the amount of petroleum and the pollutants caused by vehicular traffic are becoming greater all the time. By using hydrogen fuel cells it would be possible to reduce both of these problems.

The governments initiative is under the FreedomCAR program. Its vision is to have affordable full-function cars and trucks that are free of foreign oil and harmful emissions, without sacrificing safety, freedom of mobility, and freedom of vehicle choice. The governments main pillars for the program are listed below.

- Freedom from petroleum dependence

- Freedom from pollutant emissions
- Freedom to choose the vehicle you want
- Freedom to drive where you want, when you want
- Freedom to obtain fuel affordably and conveniently

The following figure, Fig. 18.8, illustrates one of the governments concerns.

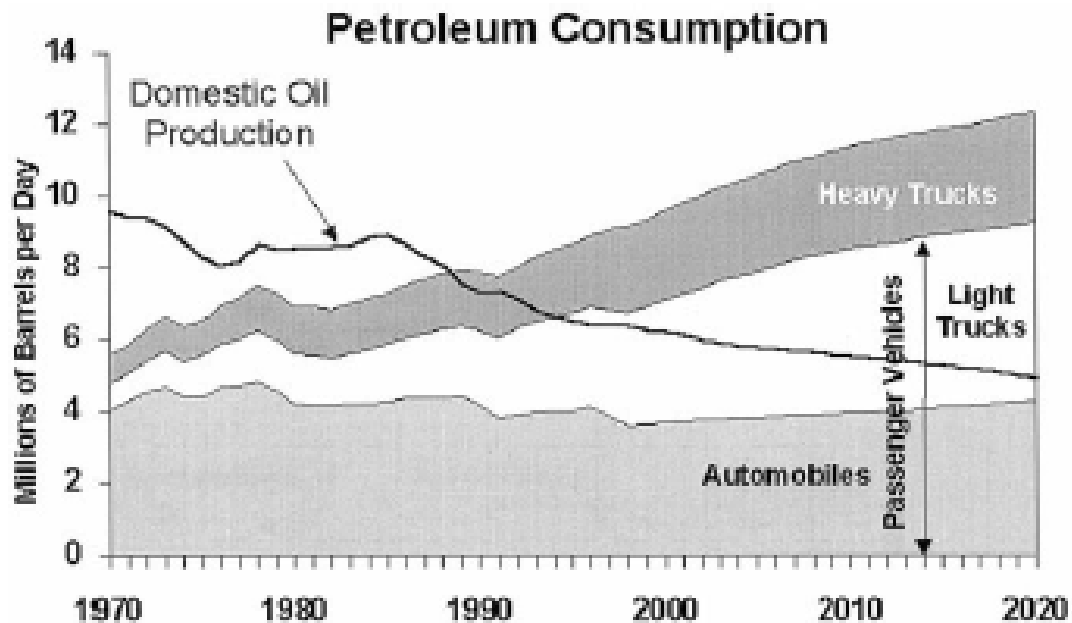


Figure 18.8: Petroleum use by vehicles in the USA

They feel that this development will have tremendous national benefits. Some of which are to ensure the nation's transportation energy and environmental future, by preserving and sustaining America's transportation freedoms. This is an idea base upon independence and security made available through technology. The government and industry research partners, which are national labs, universities, and industry, recognize that the steady growth of imported oil to meet our demand for petroleum products is problematic and not sustainable in the long term. No single effort limited to one economic sector can successfully change this trend. Altering our petroleum consumption patterns will require a multi-tiered approach, including policy and research programs, across every end use zone of our economy. The transportation sector

has a significant role to play in addressing this challenge, and success resulting from the FreedomCAR research initiatives will help accomplish the broader national goals and objectives that are being pursued [13].

Their strategic approach is to develop technologies to enable mass production of affordable hydrogen-powered fuel cell vehicles and ensure the hydrogen infrastructure to support them. Continue support for other technologies to dramatically reduce oil consumption and environmental impacts, such as other hydrogen based goods and services. Instead of single-vehicle goals, the idea is to develop technologies applicable across a wide range of passenger vehicles, thus enabling the industry to interface the new technology with all vehicles, as opposed to single new vehicles.

The technological hurdles are present, but the government feels that they can be overcome, given time and resources.

They would like to ensure reliable systems for future fuel cell power trains with costs comparable with conventional internal combustion engine/automatic transmission systems, the goals are:

- Electric propulsion system with a 15-year life capable of delivering at least 55 kW for 18 seconds and 30 kW continuous at a system cost of \$12/kW peak.
- 60% peak energy-efficient, durable fuel cell power system (including hydrogen storage) that achieves a 325 W/kg power density and 220 W/L operating on pure hydrogen.

Cost targets are:

- Internal combustion systems that cost \$30/kW, have a peak brake engine efficiency of 45%, and meet or exceed emissions standards.
- Fuel cell systems, including a fuel reformer, that have a peak brake engine efficiency of 45% and meet or exceed emissions standards with a cost target of \$45/kW by 2010 and \$30/kW in 2015.

To enable reliable hybrid electric vehicles that are durable and affordable, the goal is to develop an electric drive train energy storage with 15-year life at 300 W with discharge power of 25 kW for 18 seconds at a cost of \$20/kW. To enable this transition to a hydrogen economy it is going to be necessary to ensure widespread availability of hydrogen fuels and retain the functional characteristics of current vehicles. To meet these goals:

- Cost of energy from hydrogen equivalent to gasoline at market price, assumed to be \$1.50 per gallon (2001 dollars).

- Hydrogen storage systems demonstrating an available capacity of 6 *wt%* hydrogen, specific energy of 2000 $\frac{W-h}{kg}$, and energy density of 1100 $\frac{W-h}{L}$ at a cost of \$5/(kW - h).
- Internal combustion systems operating on hydrogen that meet cost targets of \$45/kW by 2010 and \$30/kW in 2015, have a peak brake engine efficiency of 45%, and meet or exceed emissions standards.

To improve the manufacturing base, the goal is material and manufacturing technologies for high-volume production vehicles that enable and support the simultaneous attainment of 50% reduction in the weight of vehicle structure and subsystems, affordability, and increased use of recyclable/renewable materials.

The industry and the supporting groups are pursuing all of these goals/standards in order to help get FCV on the road as soon as possible. Once these technical and regulatory barriers are achieved it will be possible to begin the development of full scale FCV integration into our society.

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