

Direct Methanol Fuel Cell

PROJECT REPORT

Submitted by

P-1145

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CERTIFICATE

This is to certify that the project report entitled

Direct Methanol Fuel Cell

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After years of fuel cell research and development, questions of “if” are finally becoming “when.” As a result, fuel cells will be to the 21st century what the steam engine was to the 19th century and the internal combustion engine was to the 20th century.

DEDICATED TO

Mr. William Grove,
the inventor of the fuel cell.

ABSTRACT

Scientists are constantly in search of alternate sources of energy that are environmentally friendly and do not deplete the earth's supply of fossil fuels. Because of their portable and rechargeable nature, fuel cells hold great potential as a future power source for everything from cars, to laptops, to cell phones.

Fuel cells produce energy by removing electrons from hydrogen fuel and transporting them to oxygen, via electrodes and an electrical circuit.

In this **project**, we investigated the workings of fuel cells, the pros and cons of the source of energy. Once the investigation was complete we built a **Direct Methanol Fuel Cell (DMFC)**. Our fuel cell uses the principle of DMFC, but employs a different fuel instead of methanol with a slightly varied electrode design.

The reason why fuel cells are commercially viable is because they are both a reliable source of energy and environment friendly.

ACKNOWLEDGEMENTS

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Chapter One

Introduction

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Introduction

The hydrogen fuel cell has received extensive attention in the scientific community and the public at large since about 1990. Although the technology is currently quite expensive, fuel cells offer significant benefits including high overall efficiency, quiet operation due to few moving parts and good efficiency over a wide range of operating points. Predicted cost reductions mean that in the near future, fuel cells could power everything from homes and vehicles to cell phones.

Although extensive research has been done into fuel cells for stationary power and for automobiles, and some research has been done for portable power applications like soldier power and devices like telephones and computers, virtually very little work has been done specifically in the field of small applications requiring under 3W of power. This is an interesting option for small applications because the market – and governments – are beginning to put a high value on options offering long life that would protect the users from changing batteries too often. Moreover, there aren't many facilities available for safe disposal of used batteries.

Five chapters comprise this report.

The first outlines the basic principle of a fuel cell and includes a description of the fuel cell characteristics. Both advantages and disadvantages of this type of power are examined.

The second chapter discusses the types of fuel cells and our choice of the type. The reasons behind our choice are explained. DMFC is chosen for the reasons of ease of operation, low cost, low temperature and minimal volume.

The third chapter describes in detail the engineering issues and science behind fuel cell technology. The design features of a general DMFC and our changes to this DMFC are discussed here. This chapter deals exclusively with the conceptual design core of our project. The next three chapters describe the hardware and software development.

The final chapter describes how these fuel cells might be brought to market. How much would a prototype cost? Could a fully-developed cell be competitive with batteries? How would fuel costs compare to batteries? The limitations and other infrastructure issues are briefly discussed in this chapter along with the applications our fuel cell can power. With the cost information finishing off the body of this report, a final summary is presented that recapitulates the findings.

What is a fuel cell?

A fuel cell is a device that generates electricity by a chemical reaction. Every fuel cell has two electrodes, one positive and one negative, called, respectively, the cathode and anode. The reactions that produce electricity take place at the electrodes.

Every fuel cell also has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which speeds the reactions at the electrodes.

Hydrogen is the basic fuel, but fuel cells also require oxygen. One great appeal of fuel cells is that they generate electricity with very little pollution—much of the hydrogen and oxygen used in generating electricity ultimately combine to form a harmless byproduct, namely water.

One detail of terminology: a single fuel cell generates a tiny amount of direct current (DC) electricity. In practice, many fuel cells are usually assembled into a stack. Cell or stack, the principles are the same.

Hydrogen

There is little doubt that Earth's climate is getting warmer. How much is due to human production of carbon dioxide and how much is due to a natural warming cycle is not certain. What can be shown, however, is that carbon dioxide emissions from internal combustion engines do contribute to global warming.

There has been much interest in the use of hydrogen as a fuel to relieve our dependence

The most promising technology to use hydrogen as an energy source is the fuel cell. Simply put, a fuel cell combines hydrogen with oxygen, producing electricity with water as a byproduct.

Working

Fuel cells are electrochemical devices that convert a fuel's chemical energy directly to electrical energy with high efficiency. With no internal moving parts, fuel cells operate similarly to batteries. An important difference is that batteries store energy, while fuel cells will produce electricity continuously as long as is supplied. Fuel cells chemically combine a fuel (normally hydrogen) and an oxidant without burning, thereby dispensing with the inefficiencies and pollution of traditional combustion systems.

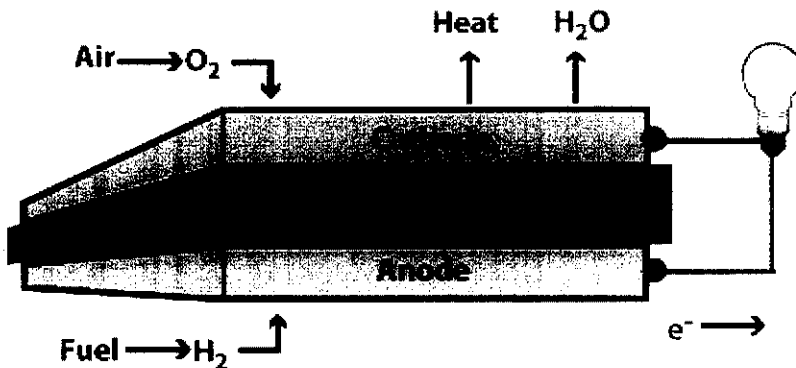


Figure 1

Fuel cells forego the traditional fuel-to-electricity production route common in modern power production, which consists of heat extraction from fuel, conversion of heat to mechanical energy and, finally, transformation of mechanical energy into electrical energy. In a sense, our bodies operate like fuel cells because we oxidize hydrocarbon compounds in our food and release chemical energy without combustion.

Fuel cells function on the principal of electrolytic charge exchange between a positively charged anode plate and a negatively charged cathode plate. When hydrogen is used as the basic fuel, "reverse hydrolysis" occurs, yielding only water and heat as byproducts while converting chemical energy into electricity, as shown in Figure 1.

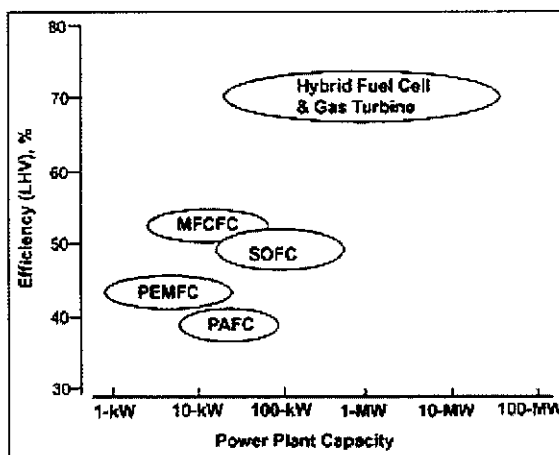
Pollutant emissions are practically zero.

Fuel Cell Benefits

Environmental Acceptability

The environmental benefits of fuel cells are some of the main motivating forces in their development. These benefits include the zero- or near-zero-emission of criteria pollutants (NO_x, SO_x, CO, and hydrocarbons) and very low noise emissions. ²

Environmentally friendly fuel cell properties could eliminate consumer contempt for power generation close to their houses and businesses. While most consumers probably would prefer to have conventional electricity generated at a location far from their homes due to the noise and pollution, the benign nature of fuel cells makes them non-offensive even if placed in residential communities.



Fuel Cell System Efficiencies

Figure 2

Depending upon fuel cell type and design, fuel-to-electricity efficiency ranges from 30 to 60 percent (LHV). For hybrid fuel cell/gas turbine systems, electrical conversion efficiencies are expected to achieve over 70 percent (LHV). When byproduct heat is utilized, the total energy efficiency of fuel cell systems approaches 85 percent.

As shown in Figure 2, stand-alone fuel cell systems have the capability of reaching efficiencies greater than 50 percent, even at relatively small sizes (e.g., 10 kW). Hence, fuel cell systems could reduce the impact of electricity production on global climate change by reducing the amount of greenhouse gases emitted into the atmosphere per kilowatt-hour of power. They would also reduce resource depletion and dependence on fossil fuels by allowing more power to be harnessed from same amount of fuel.

Oil Reserves, Transportation, and Fuel Cells

No one can predict what will happen to world wide oil prices or global oil demand. The world's production of oil reached a record level of 65 million barrels a day in 1997, and global demand is rising more than 2% a year. Americans spend roughly \$100,000 per minute to purchase foreign oil, and the U.S. transportation sector uses over 10% of the world's oil. Consumption of oil by passenger vehicles, which include automobiles and light duty trucks, exceeds all of the United States' domestic production. Reserves of fossil fuels are large but finite, and there is growing evidence to suggest that world production of crude oil will peak early in the 21st century. The Energy Information Agency forecasts that worldwide demand for oil will increase 60% by 2020. By 2010, Middle East OPEC states (Organization of Petroleum Exporting Countries), considered to be unpredictable and often unstable, will have over 50% of the world business, and the switch from growth to decline in oil production could cause economic and political tension. As excess oil production capacity begins to decline over the coming decades, oil prices can be expected to rise, and the transportation sector is likely to be most heavily affected by these fluctuations. World wide, transportation relies almost totally on oil, and there are few viable short-term fuel options.

About 25% of all human-generated greenhouse gases come from transportation — more than half of that from light-duty vehicles. Unlike air pollutants (carbon monoxide, nitrogen oxides, hydrocarbons, and particulates — soot, smoke, etc.), greenhouse gas emissions (primarily carbon dioxide, methane, nitrous oxide, water vapor, etc.) from vehicles cannot be easily or inexpensively reduced by using add-on control devices such as a catalytic converter. In addition, unlike air pollutants, greenhouse gas emissions are not regulated by the Environmental Protection Agency. The relationship between gasoline

reducing vehicle miles traveled, and switching to lower or non-carbon fuels will begin to decrease carbon dioxide emissions. The introduction of fuel cells into the transportation sector will increase fuel efficiency, decrease foreign oil dependency, and become an important strategy/technology to mitigate climate change. As fuel cell vehicles begin to operate on fuels from natural gas or gasoline, greenhouse gas emissions will be reduced by 50%. In the future, the combination of high efficiency fuel cells and fuels from renewable energy sources would nearly eliminate greenhouse gas emissions. The early transition to lower carbon-based fuels will begin to create cleaner air and a stronger international energy security.

Climate Change, Greenhouse Gases, and Fuel Cells: What is the Link?

There is a growing scientific consensus that increasing levels of greenhouse gas emissions are changing the earth's climate. The natural greenhouse gases include carbon dioxide (CO₂), water vapor (H₂O), nitrous oxide (N₂O), methane (CH₄) and ozone (O₃), and are essential if the Earth is to support life. With the exception of water vapor, carbon dioxide is the most plentiful. Since the beginning of the Industrial Revolution in 1765, burning fossil fuels and the increased energy needs of a growing world population have added man-made, or anthropogenic, greenhouse gas emissions into the environment. Carbon dioxide constitutes a tiny fraction of the earth's atmosphere — about one molecule in three thousand — but is the single largest waste product of modern industrial society. The concentration of carbon dioxide in the atmosphere has risen from about 280 parts per million by volume to the current level of over 360 parts per million by volume and anthropogenically caused atmospheric concentration of methane has doubled. In the past 100 years, levels of nitrous oxide have risen about 15%. Increasing concentrations of greenhouse gases trap more terrestrial radiation in the lower atmosphere (troposphere), artificially enhancing the natural greenhouse effect. The average temperature of the Earth has warmed about 1°C since the mid-19th century when measurements began, and fragmentary records suggest the Earth is warmer than it has been in nearly 2,000 years.

Under the most optimistic scenarios proposed by the United Nations Intergovernmental Panel on Climate Change, carbon dioxide is expected to rise to approximately 600 parts per million by volume during the next century — more than double the level held for

As per the above evidence, Carbon-di-oxide emissions are largely responsible for global warming and other related climatic changes. Hence, the use of fuel cells would obviate or if not atleast drastically reduce the CO₂ emissions that lead to global warming.

Disadvantages

While fuel cells are a promising alternative energy source, they are not yet an economically viable option for power generation.

One drawback to using fuel cells in many commercial applications (e.g. powering cars) is the cost involved with converting the existing fuel-supplying infrastructure (namely gasoline stations) to handle different fuels.

Another drawback is that some types of fuel cells have very high operating temperatures, thereby limiting the scope to applications where temperature does not affect operation.

Fuel Cells are promising, but face significant challenges for commercialization.

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Chapter Two

Fuel Cell Type

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Fuel Cell Types

Scientists and inventors have designed many different types and sizes of fuel cells in the search for greater efficiency, and the technical details of each kind vary. Many of the choices facing fuel cell developers are constrained by the choice of electrolyte. The design of electrodes, for example, and the materials used to make them depend on the electrolyte. Today, the main electrolyte types are alkali, molten carbonate, phosphoric acid, proton exchange membrane (PEM) and solid oxide. The first three are liquid electrolytes; the last two are solids. ³

The type of fuel also depends on the electrolyte. Some cells need pure hydrogen, and therefore demand extra equipment such as a “reformer” to purify the fuel. Other cells can tolerate some impurities, but might need higher temperatures to run efficiently. Liquid electrolytes circulate in some cells, which requires pumps. The type of electrolyte also dictates a cell’s operating temperature—“molten” carbonate cells run hot, just as the name implies.

Each type of fuel cell has advantages and drawbacks compared to the others, and none is yet cheap and efficient enough to widely replace traditional ways of generating power, such coal-fired, hydroelectric, or even nuclear power plants.

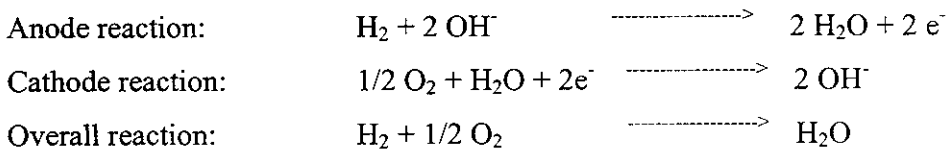
Alkaline Fuel Cell

An example : Direct Methanol Fuel Cell

Low temperature aqueous alkaline electrolyte cells have the advantage of being able to *start up easily from cold*, and operate usually at 60-80 °C, where the water vapour pressure of the electrolyte is appropriately high for a controlled removal rate. At these temperatures, *highly active catalysts are required*, usually of the platinum family. Silver and high-surface nickel have been used, however, as catalysts in these system; nickel is conventionally used as a conducting structural material.

Cheaper catalysts normally require higher operating temperatures; the Bacon cell is an example of a nickel catalyst used at 200-250 °C. At these temperatures, either a high pressure must be applied to the system or highly concentrated solutions must be used to *prevent water loss*. High-pressure systems are not suitable for air operation, due to the high pumping energy required, whereas high concentration may cause corrosion, which restricts the choice of construction materials.

The intolerance of this type of cell to carbon dioxide is a major problem; it *restricts the choice of fuel* to pure hydrogen or hydrazine, and requires that the air filter removes 0.04% of the CO₂ present in the air. The *internal reforming cell* is an attempt to get rid of this problem; the fuel electrode is made of palladium plus silver, and the fuel is either alcohol or a hydrocarbon which is reformed with steam on a nickel catalyst on one side of the electrode. The hydrogen formed passes through the electrode and reacts with the electrolyte, but the palladium prevents the CO₂ from passing through and getting into the electrolyte.



Sulphuric and Phosphoric Acid Fuel Cells

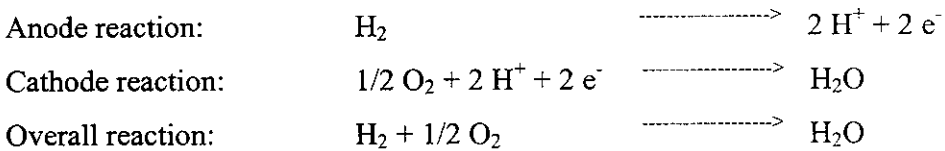
Acid electrolyte cells are *more tolerant to CO₂* and allow the use of normal air and non-pure hydrogen. But the corrosion problem restricts the choice of construction materials especially for the electrodes and the catalysts. The electrodes can be made out of gold, tantalum, titanium and carbon and only the *platinum group* metals can be used as catalysts. The acid used as the electrolyte must be *non-volatile*, such as sulfuric and phosphoric acids, so that only water is lost by evaporation.

The electrolyte in the PAFC is a paper matrix saturated with phosphoric acid, transporting the hydrogen ions. The operating temperature is around 200 °C. The operating temperature

require platinum as catalyst which is supported being dispersed on graphite material. But platinum at this temperature is sensitive to CO-poisoning.

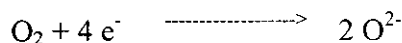
Cells, which use hydrocarbons directly as fuel around 150 °C, have low efficiency and current density, thus have been restricted to research investigations. Alcohol fuels and impure hydrogen (containing CO and CO₂ produced by reforming hydrocarbons) have been used by various companies.

In general, the performances of acid cells are *much lower* than that of alkaline cells, due to the poorer performances of the air electrode, probably because of the increased stability of formed peroxides in an acid environment. However there are many *compromises* that can be made between alkaline and acid fuel cells, considering the constructions and operating temperature and regarding the probable use of the desired cell.

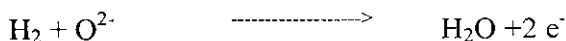


Molten Carbonate Fuel Cell

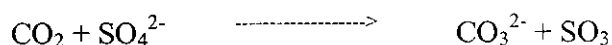
In the molten carbonate fuel cell, the electrolyte consists of a molten mixture of potassium carbonate and lithium carbonate to transport carbonate-ions from the cathode to the anode. The CO₃²⁻ transport needs supply of CO₂ at the cathode side of the cell, which is generally, be obtained by *recycling* the anode off side gas. The operating temperature is about 850 °C, which allows nickel to be used as catalyst material. The process occurring in a hydrogen-oxygen fuel cell operating at higher temperatures *without an aqueous electrolyte* might well be considered as oxide ions production at the air electrode:



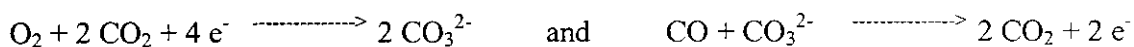
Which then move to the fuel electrode to oxidize the hydrogen:



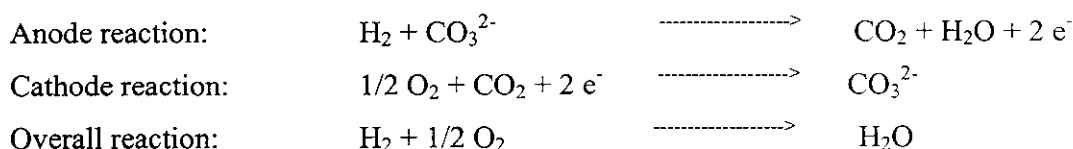
and it might therefore be considered that a molten ionic oxide would provide the best electrolyte to encourage this process. However, simple ionic oxides have melting points greater than 1000 °C and therefore attention has been focussed on salts melting at *lower temperature*. These salts are generally those with oxygen-containing anions, e.g. nitrates, sulfates, carbonates. At high temperature it is likely that the direct reaction of hydrocarbons at the fuel electrode is quite favorable and hence *conversion of petroleum* products to hydrogen or methanol is *unnecessary*. But consideration must be given to the effect of hydrocarbon oxidation at the fuel electrode on the choice of electrolyte. Carbon dioxide will be a major product that can be troublesome with some salts, for example:



Hence it is most satisfactory to consider as electrolyte a molten carbonate or mixture of carbonates. A mixture of salts may have a considerable advantage since it will have a *lower melting point* than either of its components. A convenient way of maintaining the carbonate composition of the electrolyte invariant is to remove carbon dioxide as a gaseous product from the fuel electrode and transfer it to the oxidant electrode in the air or oxygen stream. Thus for a fuel such as carbon monoxide the overall electrode processes will be:



Thus carbonate ion transfer within the electrolyte may be balanced by carbon dioxide transfer outside it. A similar mechanism could operate even for cells using hydrogen as a fuel.



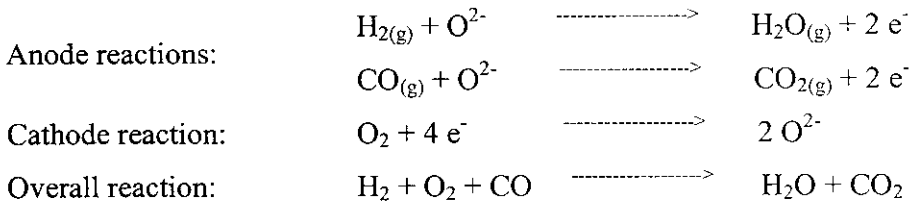
Solid Oxide Fuel Cell

Solid oxide fuel cells are constructed *entirely from solid-state materials*, using an ion-conducting oxide ceramic as the electrolyte, and are operated in the temperature range of 900-1000 °C. SOFC provide several advantages compared to other fuel cell types: they generate few problems with electrolyte management (to compare with liquid electrolytes, which are often corrosive and difficult to handle), they have the *highest efficiencies* of all fuel cells (50-60 %) and for combined heat and power applications internal reforming of hydrocarbon fuels is possible.

Current technology employs several *ceramic materials* for the active fuel cell components. The anode is typically constructed from an electronically conducting nickel/yttria-stabilized zirconia cermet (Ni/YSZ). The cathode is based on a mixed conducting perovskite, lanthanum manganate (LaMnO_3). Yttria-stabilised zirconia (YSZ) is used as the oxygen ion-conducting electrolyte. To generate a suitable voltage, fuel cells in the same stack are interconnected with a doped lanthanum chromate (eg $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$) joining the anodes and cathodes of adjacent units. Although several stack designs are being considered around the world, the most common configuration is the planar (or "flat-plate") SOFC.

The high temperature range of SOFC operation is required for the YSZ electrolyte to provide sufficient oxygen ion conductivity. However, the cost to manufacture these devices is proving to be still *very high*, primarily because expensive high temperature alloys must be used for the balance-of-plant structures. These costs would be substantially reduced if the operating temperature could be lowered to between 600-800 °C, allowing the use of cheaper structural components, such as stainless steel. A lower operating temperature would also ensure a greater overall system efficiency and a reduction in the thermal stresses in the active ceramic structures, leading to a longer expected lifetime. To lower the operating temperature of SOFC, either the conductivity of YSZ must be improved, or *alternative electrolytic materials* must be developed to replace it. A concerted effort is being made by researchers around the globe to develop such materials. Ceramics that are currently being investigated

include Gd-doped CeO_2 , $\text{Ba}_2\text{In}_2\text{O}_5$ and (Sr,Mg)-doped LaGaO_3 . However, these new materials all face serious drawbacks compared with YSZ, and it is most likely that the first commercial SOFC units will use *zirconia-based ceramics* as the electrolyte.

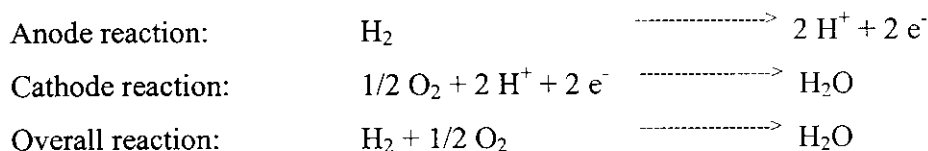


Proton Exchange Membrane Fuel Cell

The proton exchange membrane fuel cell is unusual in that its electrolyte consists of a layer of *solid polymer* which allows protons to be transmitted from one face to the other. It basically requires hydrogen and oxygen as its inputs, though the oxidant may also be ambient air, and these gases must be *humidified*. It operates at a low temperature because of the limitations imposed by the thermal properties of the membrane itself. The operating temperatures are around 90 °C. The PEMFC can be contaminated by carbon monoxide, reducing the performance by several percent for contaminant in the fuel in ranges of tens of percent. It requires cooling and management of the exhaust water in order to function properly.

There are a number of companies involved in manufacturing PEMFC. Ballard are probably the leaders, though companies such as DeNora in Italy and Siemens are progressing fast. The main focus of current designs is *transport applications*, as there are advantages to having a solid electrolyte for safety, and the heat produced by the fuel cell is not adequate for any form of cogeneration. Daimler-Benz has taken a high profile in developing cars powered by Ballard fuel cells, while Toyota has recently presented a vehicle that is using a fuel cell of their own design. Other car manufacturers, including General Motors and Ford, are actively engaged in similar developments. It now appears, however, that there is a strong possibility of using the PEMFC in *very small scale* localized power generation, where the heat could be used for hot water or space heating. There is also the possibility of a heater/chiller unit for

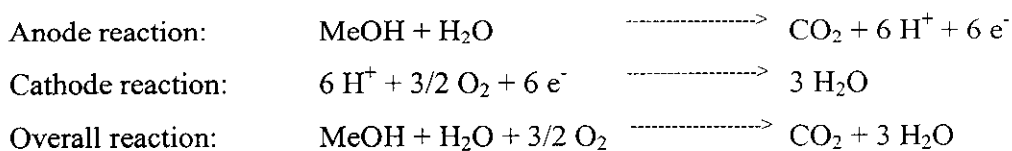
cooling in areas where air conditioning is popular. If it does prove possible to use this particular type of fuel cell for *both transport and power generation*, then the advantages generated by economies of scale and synergy between the two markets could make the introduction of the technology easier than in other cases.



Solid Polymer Fuel Cell

This type of fuel cell is based on solid polymer technology but uses methanol directly as a fuel. If it can be made to work, that would be a big step forward in the automotive area where the *storage or generation of hydrogen* is one of the big obstacles for the introduction of fuel cells. Prototypes exist, but the development is at an early stage. There are principal problems, including the *lower electrochemical activity* of the methanol as compared to hydrogen, giving rise to lower cell voltages and, hence, efficiencies. Also, methanol is miscible in water, so some of it is liable to cross the water-saturated membrane and cause corrosion and exhaust gas problems on the cathode side.

Nevertheless, the direct methanol fuel cell is an interesting proposition and a number of places are working on it, including Siemens in Germany, the University of Newcastle and Argonne National Laboratory. There are also efforts to develop a low-temperature SPFC (500 °C) that would also allow the direct use of methanol, as well as using stainless steel components. The idea is still young but intriguing.



Comparison of Five Fuel Cell Technologies

Fuel Cell	Electrolyte	Operating Temperature (°C)	Applications
Polymer Electrolyte Membrane (PEM)	Solid organic polymer poly-perfluorosulfonic acid	60 - 100	electric utility portable power transportation
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100	military space
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	175 - 200	electric utility transportation
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium and/ or potassium carbonates, soaked in a matrix	600 - 1000	electric utility
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of yttria is added	600 - 1000	electric utility

In Direct Methanol Fuel Cells, typical operating temperature is 50°C-90°C, with higher efficiency at higher temperatures. Unlike other fuel cells, the DMFC does not require a reformer, instead, the anode catalyst draws hydrogen directly from the liquid methanol.

Our Choice

Of the many fuel cell classes, the type known as "direct methanol fuel cells" (or DMFCs) is considered the most appropriate for small electronic devices.

We have developed the above said Direct Methanol Fuel Cell because of the following main aspects.

- Low working temperature expectation (around 90° C)
- No need of a separate hydrogen source

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Chapter Three Design

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Design

DMFC Working - Engineering issues

A direct methanol fuel cell works by chemically reacting methanol and air in a specific way to create a thermodynamic potential. This potential is then be used to do work in a similar manner to how a regular chemical battery is used. However since a fuel cell can simply be refilled with more fuel when it runs out, fuel cells have a competitive advantage over chemical batteries.

From a thermodynamic perspective, the electrons "want" to travel to the cathode side a specific "amount," that can be quantified as the open circuit voltage. The open circuit voltage is measured with a voltmeter across the cell set to an extremely high resistance. The thermodynamic favoring of reacting the methanol and O_2 into carbon dioxide and water forces a difference in energy to build across the electrodes until the system reaches equilibrium. Once this level is reached the components stop reacting, and no additional useful energy is produced.

Useful energy is produced by lowering the voltage across the electrode below the equilibrium value. This is done by placing a resistance on the wire connecting the two sides that is weak enough that current can flow through it. The smaller the voltage difference that is imposed on the fuel cell in this manner, the more current is produced until a proton transport rate limit is reached, after which no additional energy is produced.

Hydrogen Source

Fuel cells require hydrogen and oxygen to operate. Hydrogen can be used directly, or can be obtained from fuels containing hydrogen. These hydrocarbon based fuels, such as natural gas, methanol, ethanol, gasoline, or diesel fuel would require a fuel reformer to extract the hydrogen.

Hydrogen gas in the atmosphere is too rare to isolate at a sufficient rate, so other methods of creating hydrogen must be used. The primary three methods are the use of a reformer, a direct methanol fuel cell, or an electrolyzer. A reformer takes in hydrocarbon- or alcohol-based fuel (such as gasoline, ethanol, methanol and methane) and removes the hydrogen, creating H_2 gas. The problem with this method is that it emits CO_2 (although much less than an internal combustion engine does).

An electrolyzer breaks water molecules into hydrogen and oxygen gas, both of which are used in the fuel cell itself. This could potentially create a regenerative system, where fresh hydrogen is only needed once. The only difficulty is that the electrolyzer needs an external power source to break apart the H_2O . One possibility would be to use solar power to run such an operation.

A direct methanol fuel cell skips the reformation process completely by using a catalyst that removes the hydrogen directly from methanol fuel. This method, however, still has the same difficulty with CO_2 emissions as the reformer.

Unlike other fuel cells, which require a hydrogen source, DMFC uses a catalyst on the anode to draw hydrogen from liquid methanol (in our case $NaBH_4$), eliminating the need for a fuel reformer. Hence the name "Direct Methanol Fuel Cell". This is potentially a very attractive solution to the issues of hydrogen storage and transportation (particularly for portable applications). CO_2 emissions are absent because $NaBH_4$ does not contain carbon and the reaction product is just borax.

DMFC Catalyst Info

The chemical composition of the catalysts used in DMFC's is very important to the performance of a cell. The current configuration uses an approximate 50-50 Pt-Ru (platinum - Ruthenium) anode catalyst and a platinum catalyst at the cathode. These catalysts are often mixed with carbon black to improve spatial distribution, and may be sprayed, pressed or "glued" onto the electrode.

As with any catalyst, these catalysts speed up reactions that are already energetically favorable. In this instance it is the reduction of NaBH_4 (sodium tetra hydridoborate) at the anode, and the oxidation of protons at the cathode. Exactly how this works is a topic of controversy and the speed to which the reaction is accelerated is subject to several factors.

The anode catalyst is by far the most important of the two catalysts. This catalyst must be as effective in the conversion of NaBH_4 to hydrogen as possible for the cell to achieve maximum performance. Research into the creation of better anode catalysts is therefore one of the most important areas of research at this time.

The catalyst on the cathode side is not as important to the performance of a DMFC as is the anode catalyst at this time. However there are requirements that a catalyst must meet to be a good cathode catalyst. These properties are : it must resist poisoning from the oxidation products of methanol crossover, it should enhance the proton oxidation rate, and it should be as inexpensive for its performance as possible. These goals have been reasonably achieved with the current state of the art technology.

Derivation of Ideal Fuel Cell Voltage

Prediction of the maximum available voltage from a fuel cell process involves evaluation of energy differences between the initial state of reactants in the process ($\text{H}_2 + 1/2 \text{O}_2$) and the final state (H_2O). Such evaluation relies on thermodynamic functions of state in a chemical process, primarily the Gibbs free energy. The maximum cell voltage (E) for the hydrogen/air fuel cell reaction ($\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$) at a specific temperature and pressure is calculated [$E = -G/nF$], where G is the Gibbs free energy change for the reaction, n is the number of moles of electrons involved in the reaction per mole of H_2 , and F is Faraday's constant, 96,487 coulombs (joules/volt), the charge transferred per mole of electrons. At a constant pressure of 1 atmosphere, the Gibbs free energy change in the fuel cell process (per mole of H_2) is calculated from the reaction temperature (T), and from changes in the reaction enthalpy (H) and entropy (S)

$$\begin{aligned} G &= H - T S \\ &= -285,800 \text{ J} - (298 \text{ K})(-163.2 \text{ J/K}) \\ &= -237,200 \text{ J} \end{aligned}$$

For the hydrogen/air fuel cell at 1 atmosphere pressure and 25°C (298 K), the cell voltage is 1.23 V.

$$\begin{aligned} E &= -G/nF \\ &= -(-237,200 \text{ J}/2 \times 96,487 \text{ J/V}) \\ &= 1.23 \text{ V} \end{aligned}$$

As temperature rises from room temperature to that of an operating fuel cell ($80^\circ\text{C}/353\text{K}$), the values of H and S change only slightly, but T changes by 55° . Thus the absolute value of G decreases. For a good estimation, assuming no change in the values of H and S

$$\begin{aligned} G &= -285,800 \text{ J/mol} - (353 \text{ K})(-163.2 \text{ J/mol K}) \\ &= -228,200 \text{ J/mol} \end{aligned}$$

Thus, the maximum cell voltage decreases as well (for the standard case of 1 atm), from 1.23 V at 25°C to 1.18 V at 80°C

$$\begin{aligned} E &= -(-228,200 \text{ J}/2 \times 96,487 \text{ J/V}) \\ &= 1.18 \text{ V} \end{aligned}$$

An additional correction for air, instead of pure oxygen, and using humidified air and hydrogen, instead of dry gases, further reduces the maximum voltage obtainable from the hydrogen/air fuel cell to 1.16 V at 80°C and 1 atmosphere pressure.

An additional drop, further occurs across the electrodes and the tapping of the above maximum discussed voltage is largely dependent on the design of the fuel cell. In reality, however, the voltage that is tapped from a single fuel cell is 0.7 V. With slight improvements in design we have improved this to 0.76 V/cell.

Our Design of DMFC

The design of a direct methanol fuel cell encompasses a number of issues like selection of material for the electrodes, size of electrodes, volume of the electrolyte (and thereby the volume of the container) and the loading of the catalyst. There also arises the issue of choosing the number of fuel cells that contribute to the fuel cell stack. However, this largely depends on the power rating of the desired application. The discrepancies in the voltage or current rating that arise between the fuel cell stack and the application can be met by using a DC chopper provided the wattage requirement is met.

A direct methanol fuel cell works by chemically reacting methanol and air in a specific way to create a thermodynamic potential (in our case NaBH_4).

Electrolysis

Fuel : NaBH_4

Cathode : Manganese-di-oxide powder on a nickel mesh using carbon support.

Anode : Platinum on a nickel mesh using carbon support.

Binder used : Tar (in place of PTFE emulsion - Poly Tetra Fluro Ethylene)

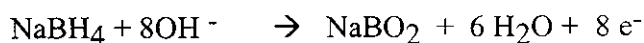
Electrolyte : KOH solution (1M / 4M) + fuel

As outlined earlier, the primary issue however lies in tapping the maximum voltage possible from a single cell.

The detailed description of the design adopted by us is given below

Chemo-Electricity:

There are two possible routes when using NaBH_4 fuel. In the first the NaBH_4 is directly oxidised, according to the equation:-



This reaction is promoted by the platinum catalyst on the electrode. However, this catalyst also promotes a reaction that produces hydrogen:-



These four hydrogen molecules then react to produce eight electrons, as shown. In either case the remarkable thing is that ONE molecule of NaBH_4 gives EIGHT electrons. This is why it is such a good fuel.

DESIGN OF ELECTRODES: AN EVOLUTIONARY PROCESS

We adopted a number of designs, for the electrodes in our fuel cells. More specifically, it was the anode design that was varied with more intensity throughout the length of the process. Two cathode designs were also tried.

ENDEAVOR 1:

a) Cathode design:

Our cathode consisted of a Stainless Steel (S.S) mesh that was coated with a mixture of manganese dioxide and carbon. The reason why we used Stainless Steel in place of the conventional nickel was because of the commercial difficulty of obtaining nickel. Stainless Steel, that contains 20% nickel was a ready replacement. It is easily obtainable, owing to its

wide usage in mosquito nets and other applications. We also placed an order for a nickel mesh with Himedia laboratories , Mumbai.

Ideally, manganese in place of manganese dioxide would have served the purpose better. However, owing to the fact that manganese in its pure form is not easily available, we replaced manganese with manganese dioxide. We used the conventional binder that is used to coat the nickel mesh with manganese/manganese dioxide is PTFE (Teflon).

The procedure for binding manganese dioxide/Carbon mixture with Stainless Steel is now briefly outlined:

- 1) The binder (Teflon) is mixed with Manganese dioxide and made into a paste.
- 2) The paste is then smothered on the Stainless Steel mesh evenly.
- 3) The mesh is then neatly pressed by placing it in a specially prepared dye, that has the dimensions of the mesh.
- 4) It is then allowed to dry.

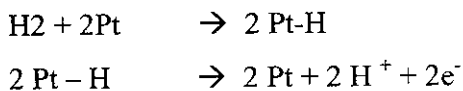
On using this, we obtained a voltage of 0.3 volts/cell. Furthermore, the manganese dioxide powder along with carbon started falling off the nickel mesh (in small quantities) over a period of 4-5 hours.

On experimenting with tar in place of Teflon, we found that the voltage obtained per cell remained the same. However, there was a significant difference in the fact that the mixture was bound well and was not falling off. Hence we opted for Tar in all our future endeavors.

b) Anode design:

The half reactions occurring at each electrode can only occur at a high rate at the surface of the Pt catalyst. Platinum is unique because it is sufficiently reactive in bonding H and O intermediates as required to facilitate the electrode processes, and also capable of effectively releasing the intermediate to form the final product. For example, the anode process requires

Pt sites to bond H atoms when the H₂ molecule reacts, and these Pt sites next release the H atoms, as H⁺ and e⁻.



This requires optimized bonding to H atoms — not too weak and not too strong — and this is the unique feature of a good catalyst. Realizing that the best catalyst for the polymer electrolyte membrane fuel cell is expensive, lowering Pt catalyst levels is an on-going effort. One of the best ways to accomplish this is to construct the catalyst layer with the highest possible surface area. Each electrode consists of porous carbon (C) to which very small Pt particles are bonded. The electrode is somewhat porous so that the gases can diffuse through each electrode to reach the catalyst. Both Pt and C conduct electrons well, so electrons are able to move freely through the electrode. The small size of the Pt particles, about 2 nanometers in diameter, results in an enormously large total surface area of Pt that is accessible to gas molecules. The total surface presented by this huge number of small particles is very large even when the total mass of Pt used is small. This large Pt surface area allows the electrode reactions to proceed at many Pt surface sites simultaneously. This high dispersion of the catalyst is one key to generating significant electron flow, i.e. current, in a fuel cell.

The conventional anode design consists of a platinum catalyst, in the form of a powder, dispersed in carbon powder for maximum surface area exposure. This is then made into a paste with Teflon, and then smothered on the mesh. The problem with this design, we thought, was that the net resistance of the electrode is high.

ENDEAVOR 2:

Both the electrodes in this endeavor were made of nickel mesh. To make sure that we have an improved material we fabricated electrodes using the same design and found that we obtained 0.38 volts/cell. Hence, we decided to use nickel in place of stainless steel in all our future designs, the second endeavor onwards.

a) Cathode design:

In addition to the change of material, there was another major change in the cathode. We reasoned that the addition of carbon to manganese dioxide would increase the net resistance of the cathode, causing a small voltage drop to appear across it. Thus we decided to try using a cathode which has only the manganese dioxide paste smeared across it. After fabricating an electrode of this kind, we compared its performance with that of the previous cathode, using the same anode as reference. We found that our reasoning was right, and the net voltage of the single cell increased to 0.48. this design was hence adopted in our final model as well.

b) Anode design:

After achieving the above satisfactory cathode design, we moved on to the design of the anode. Using the same reasoning - minimizing the net resistance of the circuit - we decided to use a naked nickel mesh clipped with platinum, instead of coating it with carbon. After preparing such an electrode, we compared its performance with the previous anode using the above prepared cathode as reference. The net voltage that was obtained per cell now increased to 0.55 volts/cell. Thus, an even better anode design was obtained and incorporated.

ENDEAVOR 3:

In our final endeavor, we used the same reasoning to try and improve the performance of the cell even further. However, the design of the cathode remained the same. We could not minimize the resistance of the surface, as the manganese dioxide powder needed mechanical support to be fixed into the cell. Moreover, the later realized that the use of nickel as a current collector could not be neglected.

Anode design:

The anode design was modified even further in an attempt to reduce the resistance of the anode even more. The new design consisted of the nickel mesh being fully removed from the anode. A thick platinum wire as simply used as the electrode. However, on using such an electrode we found that the voltage of the cell actually reduced, if the same amount of platinum that was used as used earlier was employed. Even if a slightly higher voltage is obtained using a lot more platinum, such a fuel cell would not be cost efficient. Moreover, only the hydrogen that is actually produced by the reactions between the electrolyte and the fuel (NaBH_4) can actually be ionized by the platinum, any further use of platinum would be unnecessary. Moreover, it is of utmost importance that the free electrons are collected and made to flow across the load. This cannot be compromised on, as then any improvements in designs would run a waste and the very purpose of the cell would be violated. The voltage of the fuel cell using this design was found to be 0.51 volts/cell.

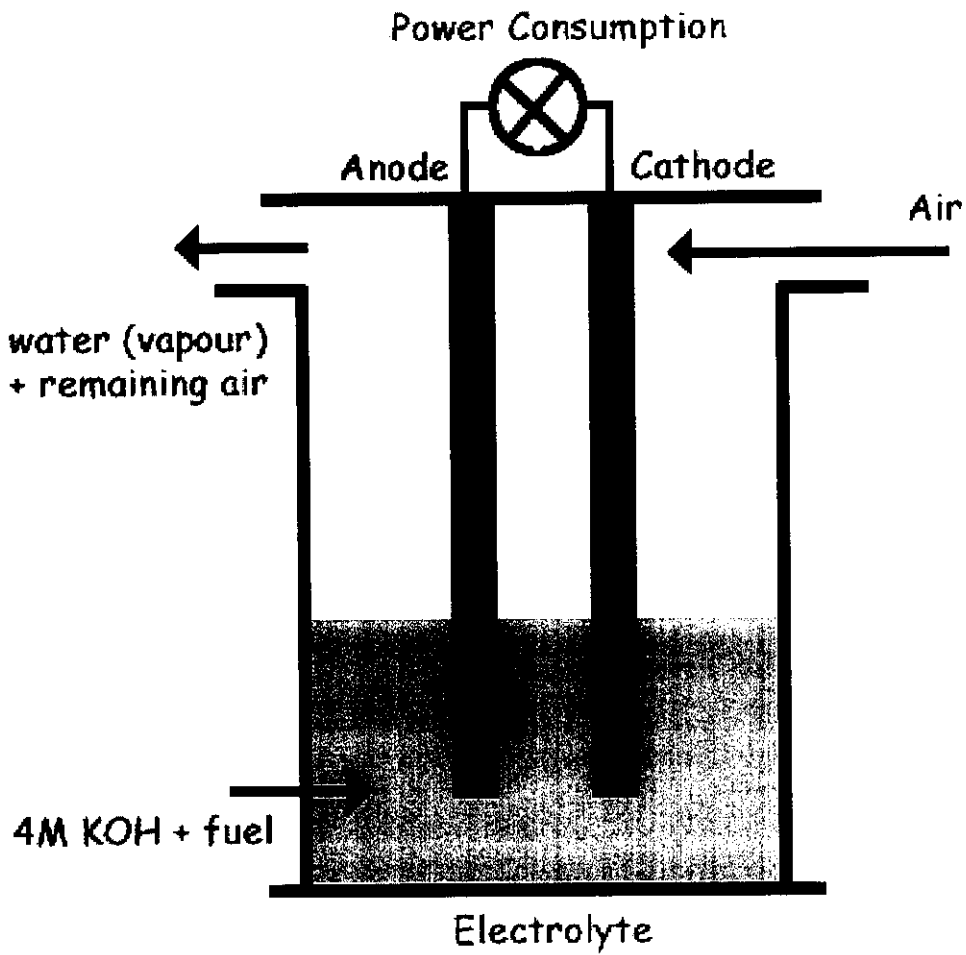
Though endeavor three failed, there is a lot of scope for research in this area. For instance, the exact amount of the mesh to be used for current collection could be found out. Thus, while tapping maximum current from the circuit the resistance of the circuit can also be minimized.

Another issue worth mentioning is that the current collection ability of the electrode increases with its size. Moreover, in spite of the increase in size it is worth remembering that only the hydrogen ions produced can be converted to water. Hence after a certain dimension, the increase in the size of the cathode would be futile.

VOLUME OF THE ELECTROLYTE:

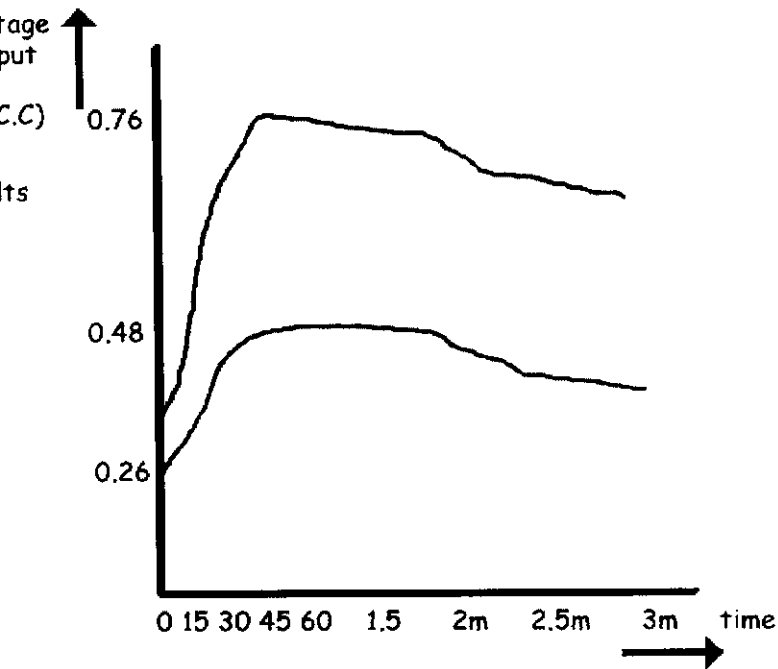
The volume of the electrolyte we use is about 25 cm cube. This was primarily done to decrease the size of the cell and thereby the stack. Since, the volume of electrolyte is low, the electrolyte gets exhausted faster. In order to compensate for this, we increased the concentration of the electrolyte to 8 M from 4M. As common sense suggests, this provides an increased number of potassium hydroxide molecules and hence the fuel lasts longer. However, there also lies the issue of corrosion when we increase the concentration of the electrolyte. This is where the tar we use comes in handy and provides stability to the electrode of the fuel cell.

SETUP:



■ Platinum

Voltage Vs Time Plot:



- Nickel mesh and a small increase in platinum surface area
- S.S mesh (20% nickel)

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Chapter Four Conclusion

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Conclusion

Social Relevance of the project:

To put in plain words, fuel cells chemically combine hydrogen and oxygen gasses to form water and electricity.

A fuel cell is quiet, efficient and clean. Fuel cells usually run on pure hydrogen gas, which can be produced cleanly from solar power, as well as other renewable energy sources. Fuel cells running on hydrogen produce no pollution; the only byproduct is pure water. Fuel cells are about 50% efficient, while internal combustion engines are only 12%-15% efficient. And, since there are no moving parts, fuel cells can be very reliable and make almost no noise.

Fuel cells are very reliable; they have no moving parts, so they won't wear out. The fuel cells used in the space program have been running in the real world for years without failure.

Hydrogen can actually be safer than gasoline and other petroleum products. For one thing, hydrogen is a very light gas, and so if there is a leak, it tends to drift upward very quickly, even through tiny cracks in a roof, and disperse into the upper atmosphere where it is harmless. Hydrogen is also completely non-toxic; it is impossible to contaminate anything with spilled hydrogen.

Gasoline and other fossil fuels are a great source of energy; they are very compact and there is a readily available but limited supply on Earth. However, gasoline, as well as other petroleum fuels like diesel and propane, are made from fossil fuel--oil formed by tiny animals that died millions of years ago and were buried under the ground. This is a problem for two reasons: First, there is a limited supply of oil in the Earth, and at the rate we are using it now, it will almost certainly have run out by the end of the next century, possibly much sooner. The other problem is carbon; when you burn a fossil fuel, it releases carbon, along with other pollutants, into the atmosphere. This is one cause of smog in cities, and it is

unhealthy for both humans and the environment in general. Most scientists also believe that the burning of fossil fuels is causing global warming.

Solar power is a clean, nearly limitless source of electricity, but there is one disadvantage: the sun goes down at night. To solve this problem in the past, systems have used large banks of batteries, but these batteries have limited storage capacity, are very heavy, may use toxic chemicals, and must be replaced every few years.

In place of a battery, a combination electrolyzer/fuel cell system can be used. An electrolyzer uses electricity (from the solar panels) to split water into hydrogen and Oxygen atoms. The hydrogen atoms can then be stored in tanks, and that hydrogen can later (when it is cloudy or the sun is down) be used in a fuel cell to produce clean, quiet power.

By generating electricity with solar power, or other renewable power sources like wind, and then storing it for use in a fuel cell, we can greatly reduce the release of carbon into the atmosphere, as well as our dependence on the Earth's finite supply of oil.

LIMITATIONS:

1) To run any application, the usage of a DC chopper is imperative. This is so because even though the wattage requirement is met, either the voltage or the current is in excess and the other is below the requirement. Yet, their product may produce the required wattage. In our case, the current rating is far too low and the voltage rating is more than required. Hence, a chopper is a must.

Having said this, designing a chopper for such an application still involves a lot of time. Since developing a fuel cell is a tedious process in itself, we did not find time to design a chopper for a particular application.

2) Water management is key to effective operation of a fuel cell. Although water is a product of the fuel cell reaction, and is carried out of the cell during its operation, both the fuel and air entering the fuel cell must still be humidified. Too little water prevents the electrolyte from conducting the H^+ ions well and the cell current drops. If the air flow past the cathode is too slow, the air can't carry all the water produced at the cathode out of the fuel cell, and the cathode "floods." Cell performance is hurt because not enough oxygen is able to penetrate the excess liquid water to reach the cathode catalyst sites. Hence a small pump that runs on part of the output is required. This would ensure the circulation of the fuel/electrolyte mixture and would prevent flooding.

FUTURE WORK:

Future work on this topic would move the conceptual design and feasibility test presented here to more applied design work and prototype construction. The performance presented here is unlikely to be far from actual results, and assumptions made here have always erred on the side of more waste and worse performance. So building a prototype fuel cell power system – and obtaining more detailed data on the parasitic power would be an excellent way to measure real-world performance, which for the reasons outlined above is expected to be higher than the conservative estimate here. System integration of the various heat flows and physical assembly of the variously-shaped parts also needs to be demonstrated.

COSTS:

The main purpose of the project is to analyze the technical merits of the proposed fuel cell. However, the fuel cell will never be practical unless it can be affordable as well. This section attempts to assess various issues contributing to the eventual adoption of commercial fuel cell : price of the components and operating costs, in terms of fuel.

The fuel cell we built cost us INR 4200 (to date).

The main costs were that of Platinum and the fuel NaBH_4 .

NaBH_4 . -- HiMedia Laboratories, Mumbai RM 840 (100 g)

Cost : INR 1125.00

Platinum -- 1.15 g

Cost : INR 2350.00

KOH -- Potassium Hydroxide Purified Pellets (MERCK) 500g

Modern Scientific, Coimbatore

Cost : INR 185.00

The Platinum is not depleted in anyway. Only thing that gets depleted is NaBH_4 . Thus there is only the initial cost which is mostly comprised of the cost for Platinum. The running cost is very less. The same setup can be used throughout.

The need for recharging is eliminated. When the output reduces to a lower value, it is evident that the fuel has depleted and the only thing that has to be done to get the cell back running is add a few grams of fuel.

We undertook cost-reduction measures and have currently loaded the cell with optimum amount of Platinum and have also successfully reduced the size of the cell.

Thus our DMFC is by principle a DMFC but uses NaBH_4 as fuel. We have mainly focussed on the economic viability of the project and have selected the optimum usage the components and chemicals to achieve efficient and low-cost fuel cell design.

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