

# **FUEL CELLS**

**By**

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# **CHAPTER 1**

## **INTRODUCTION**

The last two decades of the 20<sup>th</sup> century can be considered as a transition time for the methods of energy production, storage and conversion. The fossil fuels, coal, oil and natural gas, which were responsible for the development of technology and mobility of mankind. It was always feared that rapid usage will result in disappearance of fossil fuels and this would stop the future progress of technology.

The dilemma is caused by the realization that previous concept of unlimited energy available through nuclear power generation turned out to be a very dangerous proposition. The situation is worsened by the fact that the hopes of a substantial global energy fraction supplied by solar energy, or other even smaller renewable sources are also unrealistic.

### **HISTORIC TRENDS**

The idea of converting chemical energy of fossil fuels directly into electricity already existed around the 1900, and resulted in large-scale experiments trying to oxidize coal and coal gas electrochemically in “piles”. The demise of all these attempts was caused by material problems. The designs of these systems were very poor and their operating lifetime was short.

After 1920, gas-diffusion electrode was recognized as the key for successful low temperature operations. A.Schmid was the pioneer who built the first

platinum-catalyzed, porous carbon-hydrogen electrodes in tubular form. Paired with air electrodes of a similar design, practical fuel cells were built. The Second World War stopped most of the research in the area of direct energy conversion.

In 1968, NASA came up with an alkaline fuel cell system, which enabled men to fly to the moon. In 1970, K.Kordesch built a hydrogen fuel cell, which was operated for 3 years in city traffic.

The membrane fuel cell system appeared as the most attractive object for development. High power densities were obtained as a result of new membrane types and catalyst research.

Hydrogen plays an important role in industrial scenarios as an energy carrier. With respect to safety, hydrogen is in the same range as that of gasoline, methane and propane. The general drawback is that hydrogen must be transferred in pipes, stored as a compressed gas. The alternative choice is the chemical production from other h containing fuels by reforming. These fuel carriers can be natural gas, alcohols – methanol or ammonia.

From today's perspective, the present status of an industrialized world requires new approaches to solve most urgent energy and environmental problems. Fuel cell technology - seems to offer promising, sustainable options for the future energy scenario. Though fuel cells have been in existence for over 160 years, recent commercialization is driven by an increase in their efficiency; an increasing consciousness of the pollution

caused by traditional fuels, a deregulation of energy markets and a realization that world oil supplies are declining.

Fuel cells are power-generating devices having a wide range of applications including stationary power generation (MW), portable power generation (kW) and transportation (kW). In a fuel cell, since the chemical energy of the fuel is directly converted to electricity, a fuel cell can operate at much higher efficiencies than internal combustion engines, extracting more electricity from the same amount of fuel. Fuel cells are capable of converting 40% of the available fuel to electricity. This can be raised to 80% with heat recovery. The fuel cell itself has no moving parts, offering a quiet and reliable source of power.

Fuel cell system efficiency is independent of the rated power above 100 kW, unlike oil, gas or coal burning power plants, where the efficiency is constant only at the megawatt power level. Even at the 40% of the rated load, a fuel cell has almost the same efficiency as that of the full load. A fuel cell responds rapidly to sudden increase or decrease in power demands. Its ability to increase output quickly is known as its spinning reserve capability, and its ability to decrease output quickly is known as its load following capability. Fuel cells are able to respond fast to load changes, because the electricity is generated by a chemical reaction. For instance, Phosphoric Acid Fuel Cell system (PAFC), can match a demand that varies by more than half its rated power within 0.1 second. Since customer's demands for electricity are not always constant, the fast response capability makes fuel cells ideal for applications such as load following and for back-up power for photovoltaic power systems, without the loss of high efficiency.

Further, fuel cell power plants are more reliable than conventional power generation. On-site fuel cells are ideally suited for electronic equipment and computers that are sensitive to voltage surges, frequency noise, and other electric interferences because they provide reliable and grid- interference free power supply. Fuel cell systems are environmentally benign. They are relatively quiet and generate little or no air pollution. The only emission from fuel cell is water when hydrogen is fed to the fuel cell. Virtually no sulphur oxides and volatile organic compounds are emitted. Fuel cells also have the ability to reduce the greenhouse gas CO<sub>2</sub> as they are more efficient and consume lesser fuel. Methane emissions from landfills can also be reduced by capturing them for use in a fuel cell. Hence fuel cell systems are ideal for power generation in remote areas.

## **OUTLOOK**

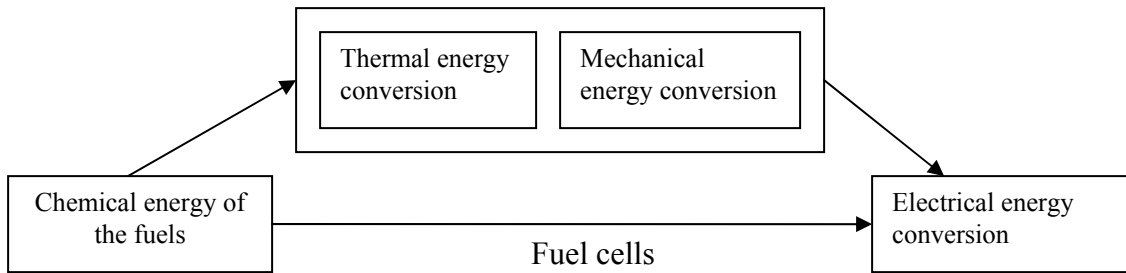
Electric vehicles operated by fuel cells are visualized as the way to meet the growing human mobility requirements worldwide. PAFC, MCFC and SOFC have a potential to demonstrate quantum leaps in improvements and can become operative by 2010. It has been predicted that by 2020 most (50%) of the automobiles will be powered fuel cell systems.

**CHAPTER 2**  
**PRINCIPLES OF A FUEL CELL**

A fuel cell is an electrochemical cell, which can continuously and directly convert the chemical energy of a fuel and an oxidant to electrical energy by a process involving essentially electrode-electrolyte system.

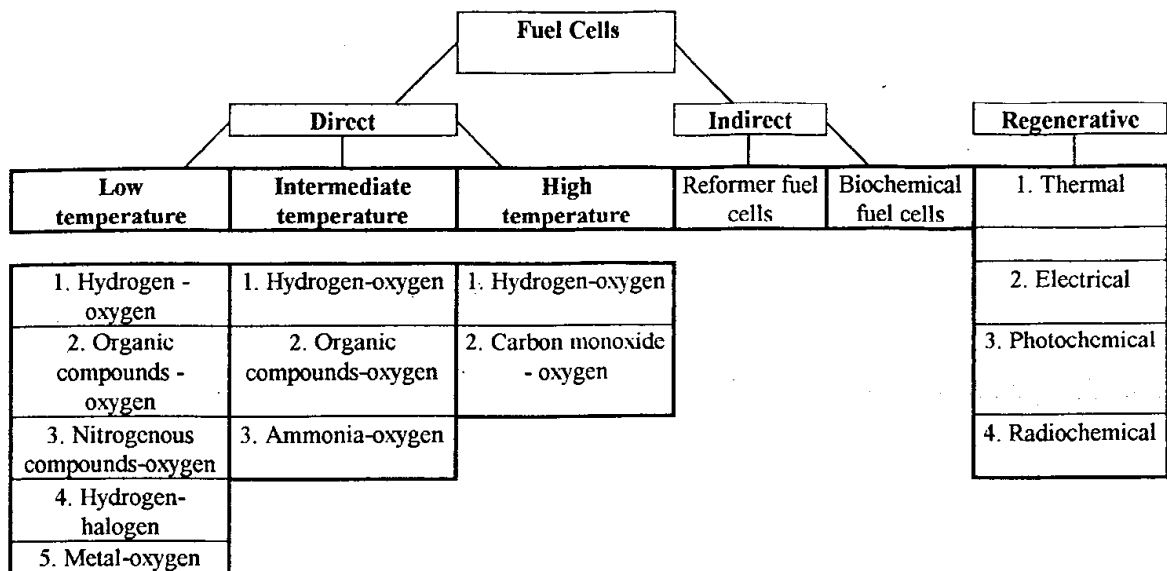
The basic principles of a fuel cell are those of the electrochemical batteries. The big difference is that, in the case of batteries, the chemical energy is stored in the substances located inside them. When this energy has been converted to electrical energy, the battery must be thrown away or recharged appropriately. In a fuel cell, the chemical energy is provided by a fuel and an oxidant stored outside the cell in which the chemical reactions take place. As long as the cell is supplied with the fuel and oxidant, electrical power can be obtained.

FUEL CELL	PRIMARY CELL	SECONDARY CELL
1. Chemical reaction producing electricity	One-way chemical reaction producing high electricity	Reversible chemical reaction producing or using electricity
2. High efficiency	Moderate efficiency	Low efficiency
3. Highly compact	Moderate size	Bulky



Direct Energy conversion in Fuel cells compared to conventional indirect technology

### CLASSIFICATION OF FUEL CELLS



In direct fuel cell, hydrogen is fed directly as fuel at the cathode and it is further classified as low (25°C-100°C), intermediate (100°C-500°C), high (500°C-1000°C) and very high temperature (above 1000°C) fuel cells depending up on the temperature of operation. In the case of indirect fuel cell, the active fuel is obtained from a source and oxidized, example hydrogen obtained by hydrocarbon cracking. When fuel is reformed by using reformer internally or externally it is known as reformer fuel cells and

when this conversion is carried out by bacteria, enzymes and algae it is known as biochemical fuel cell. In biochemical fuel cells, sulphur containing compounds are biodegraded to form  $H_2S$  and  $O_2$  containing wastes are biodegraded to form  $O_2$ , which is then used in this fuel cells. In regenerative fuel cells, fuel is used again and again through regeneration, which is done by an external agency. Energy is consumed in the regeneration. Fuel is regenerated from the products by thermal, electrical, photochemical or radiochemical methods. For practical reasons fuel cell systems are simply distinguished by the type of electrolyte used and following names and abbreviations are used: Proton Exchange Membrane Fuel Cells (PEMFC), Alkaline Fuel Cells (AFC), Direct Methanol Fuel Cells (DMFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Solid Oxide Fuel Cell (SOFC). Subsequent classifications are discussed with the system.

The fuel cells offer advantages and efficiency reliability and economy cleanliness unique operating characteristics planning flexibility and future development potentials.

### **Efficiency**

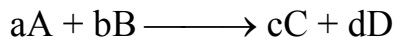
Fuel cells can convert upto 90% of energy contained in its fuel into useable electric power and heat. Current PAFC designed offer 42% conversion efficiency. It is predicted that MCFC may achieve electrical efficiencies > 60%. As the fuel cells contain fewer moving parts they have higher reliability than ICE. They cannot experience a catastrophic breakdown as can occur with ICE when the rotating parts fail.



The quiet electrochemical nature of fuel cell eliminates many of the noise associated with conventional energy systems. No ash or large volume wastes are produced from fuel cell operations. They are among the least hazardous methods of energy conversion due to their comparatively small size, the absence of a combustion engine. The electrochemical reaction of a fuel cell produces water as by product, the quantity being comparatively lower than conventional fossil fuel powered energy systems.

**CHAPTER 3**  
**THERMODYNAMICS OF A FUEL CELL**

For any reaction



The Gibbs free energy change is given by the equation

$$\Delta G = c\mu_c + d\mu_d - d\mu_a - d\mu_b$$

where  $\mu$  is the chemical potentials of the indicated species. The free energy change of a chemical reaction is a measure of the maximum amount of non-expansive net work that can be derived from the reaction. In reactions involving gases the entropy change when the number of moles of reactants and products are equal is effectively zero, this is because the main contribution to the entropy change is a change in translational entropy and this is nearly zero for a reaction involving no change in number of molecules in gas phase.

**Standard free energy change**

Chemical potential may be expressed as a function of its concentration by the relation

$$\mu = \mu_o + RT \ln A$$

for a process with constant temperature and pressure at equilibrium, the free energy change is zero.

Relation between free energy change and cell potential According to I law of thermodynamics,

$$\Delta H = q - w + P\Delta V$$

where  $\Delta H$  is the enthalpy change,  $q$  - the energy of heat absorbed and  $W$  the non expansive net work derived from the system. The maximum electrical work that can be done is a function of the no of electrons transferred in the cell. In cases where internal resistance of the cell and over potential losses are negligible, the expression for electrical work can be give by

$$W = nF(V_f - V_i)$$

as the only forms of work derived from an electro chemical system are electrical work and work of expansion total work is the sum of these two quantities. Hence

$$\Delta G = -nF(V_f - V_i)$$

as the free energy change gives the maximum amount of non-expansive work derived from a system. The electromotive force of a cell is the difference between the potentials of final and initial states. Therefore,

$$\Delta G = -nFE$$

### **Dependence of E with Temperature and Pressure**

From thermodynamics;

$$\frac{\partial G}{\partial T} = -\Delta S, \quad nF \frac{\partial E}{\partial T} = -\Delta S$$

If the entropy changes of a cell reaction are known, the potential variations can be known.

### **Variations with Pressure:**

$$E = E_o - \Delta n \frac{RT}{nF} \ln \frac{P}{P_o}$$

It is assumed that all of the reactants and products obey ideal gas laws.

More generally

$$E = E_o - \Delta n \frac{1}{nF} \int_{P_0}^P \Delta V dP$$

According to this equation it follows that reversible cell potentials for reactions involving solids and liquids are too small. In the case of gaseous reactants and products the volume change is significant and pressure effects must be taken into account.

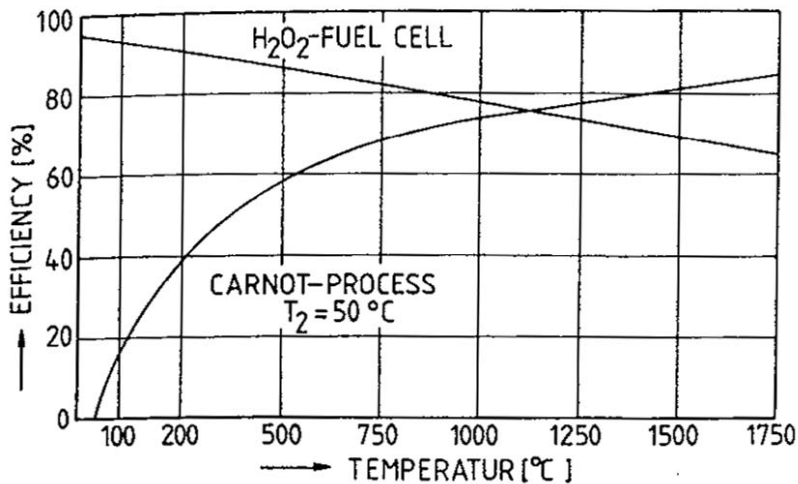
### **Electrode Polarization (over voltage):**

The losses in the galvanic elements under the conditions of delivering current conditions of delivering current are determined by kinetics of electrode reaction and kind of electrolyte used. These losses are known as polarization. The ionic mobilities of reaction partners influence the magnitude of polarization. Polarization or over voltage is the voltage difference which is measured between open circuit voltage and terminal voltage under the conditions of current flowing in either direction. On discharge the terminal voltage is lowered and on charging the terminal voltage is higher than the open circuit voltage.

Useful amounts of work are obtained from a cell when a reasonably large current is drawn but the cell potential will be decreased from its equilibrium potential because of irreversible losses. .

# THERMODYNAMIC EFFICIENCIES OF CANDIDATE FUEL CELLS

Fuel	Reaction	n	$-\Delta H^0$ [kJ/mol]	$-\Delta G^0$ [kJ/mol]	$E^0$ rev. [V]	%
Hydrogen	$H_2 + 0.5 O_2 \longrightarrow H_2O_{(l)}$	2	286.0	237.3	1.229	83.0
	$H_2 + Cl_2 \longrightarrow 2 HCl_{(aq)}$	2	335.5	262.5	1.359	78.3
	$H_2 + Br_2 \longrightarrow 2 HBr$	2	242.0	205.7	1.066	85.0
Methane	$CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O_{(l)}$	8	890.8	818.4	1.060	91.9
Propane	$C_3H_8 + 5 O_2 \longrightarrow 3 CO_2 + 4 H_2O_{(l)}$	20	2221.1	2109.9	1.093	95.0
Decane	$C_{10}H_{22} + 15.5 O_2 \longrightarrow 10 CO_2 + 11 H_2O_{(l)}$	66	6832.9	6590.5	1.102	96.5
Carbon monoxide	$CO + 1.5 O_2 \longrightarrow CO_2$	2	283.1	257.2	1.066	90.9
Carbon	$C + 0.5 O_2 \longrightarrow CO$	2	110.6	137.3	0.712	124.2
	$C + O_2 \longrightarrow CO_2$	4	393.7	394.6	1.020	100.2
Methanol	$CH_3OH + 1.5 O_2 \longrightarrow CO_2 + 2 H_2O_{(l)}$	6	726.6	702.5	1.214	96.7
Formaldehyde	$CH_2O_{(g)} + O_2 \longrightarrow CO_2 + 2 H_2O_{(l)}$	4	561.3	522.0	1.350	93.0
Formic acid	$HCOOH + 0.5 O_2 \longrightarrow CO_2 + H_2O_{(l)}$	2	270.3	285.5	1.480	105.6
Ammonia	$NH_3 + 0.75 O_2 \longrightarrow 0.5 N_2 + 1.5 H_2O$	3	382.8	338.2	1.170	88.4
Hydrazine	$N_2H_4 + O_2 \longrightarrow N_2 + 2 H_2O_{(l)}$	4	622.4	602.4	1.560	96.8



## METHANOL

Methanol is a valuable component of special motor spirit; and it was originally named 'wood alcohol', since it was derived from the destructive distillation of wood. Methanol can be produced synthetically using coal gas or water gas at high pressure and temperature in the presence of metallic catalysts, with general reaction.



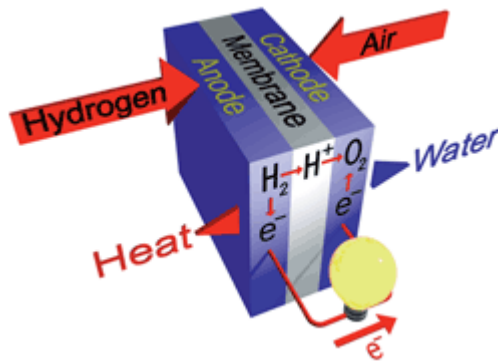
It can also be synthesized directly by the passage of synthesis gas ( $H_2+CO$ ) over a  $ZnO/Cr_2O_3$  catalyst at  $400^\circ C$  and 150-200 atm. The plant must be protected by copper lining or by the use of stainless steel from the action of the CO, which under these conditions produces iron carbonyls. The product is a mixture of 75% methanol, with very little ethanol, and 25% higher alcohols.

## CHAPTER 4

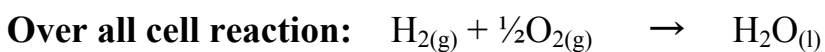
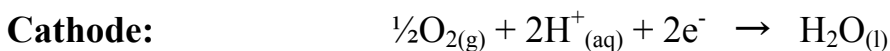
### TECHNOLOGICAL ROUTES

#### **Proton Exchange Membrane Fuel Cell (PEMFC)**

Proton exchange membrane fuel cells (PEMFCs) have reached the stage of being in the forefront among the different types of fuel cells. In 1950's Grubb suggested the use of ion-exchange polymeric membrane as the electrolyte for fuel cells. The membrane is nonpermeable to the reactant gases, hydrogen and oxygen but permeable to hydrogen ions, which are the current carriers in the electrolyte.



Electrochemical reaction occurring at the electrodes is as follows:



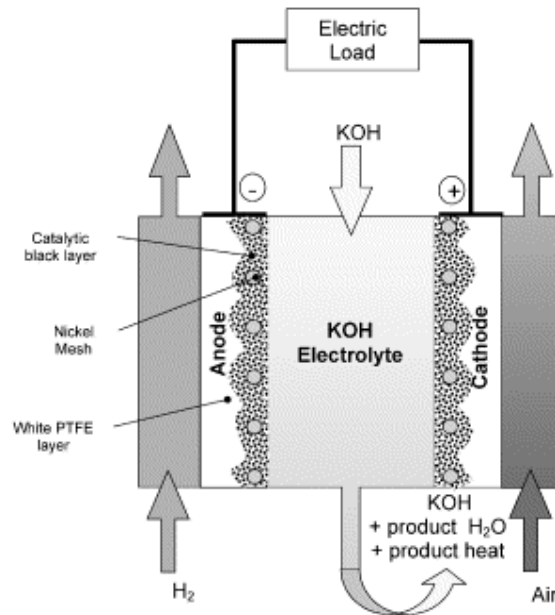
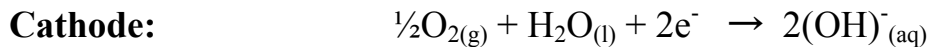
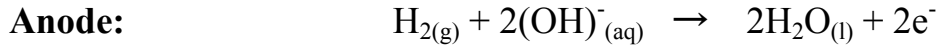
Hydrogen from the fuel gas stream is consumed at the anode, yielding electrons and hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines with electrons from the cathode and hydrogen ions from the electrolyte to produce water. Water does not dissolve in the electrolyte and instead it is carried out of the fuel cell by excess oxidant flow.

### **Alkaline Fuel Cell (AFC)**

Alkaline Fuel Cells (AFC) were developed for space use in the 1960's because of their ability to operate over a wide temperature range. It consists of two porous electrodes with liquid KOH electrolyte between them. The hydrogen fuel is supplied to the anode electrode, while oxygen from air is supplied to the cathode. The working temperature ranges from 293 to 363 K. The electrical voltage between the anode and the cathode of a single fuel cell is between 0.9 V and 0.5 V depending on the load and the electrochemical reactions taking place at these electrodes. The hydrogen is usually compressed and the oxygen is obtained from the air. It uses a circulating liquid alkaline electrolyte, potassium hydroxide (30-45% KOH). This is an effective heat transfer and water management medium. The fuel cell can produce power at ambient temperatures but is designed to deliver full power at about 343 K, which, with electrical heating, it will normally reach within 10 min of a cold start.

The cell reactions are as follows:

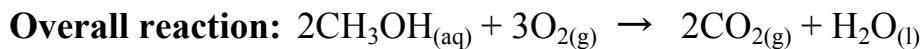
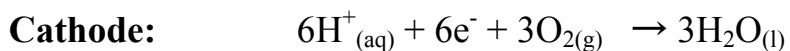
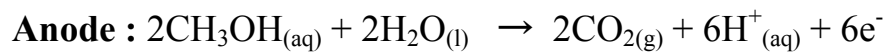
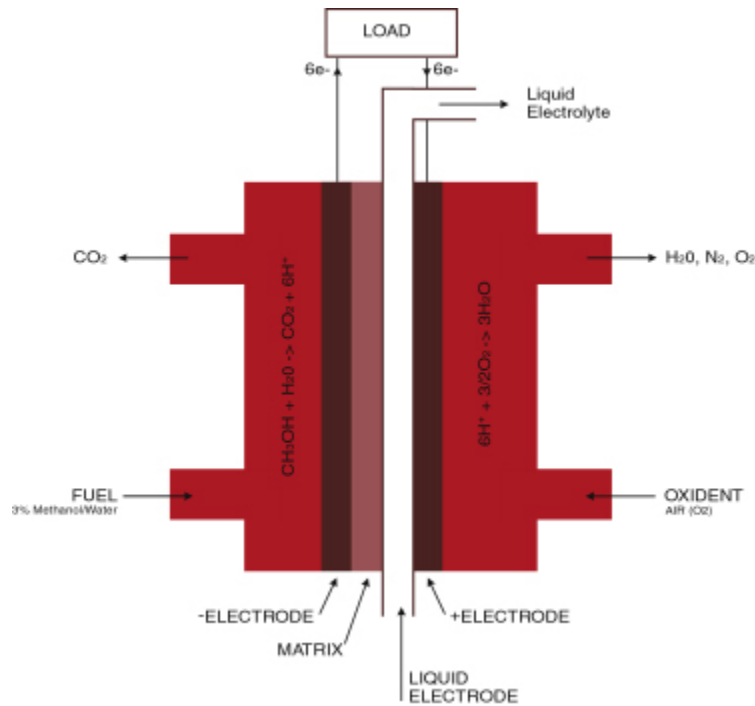




## Direct Methanol Fuel Cells (DMFC)

DMFC is essentially the same as a PEMFC, but in DMFC, methanol is fed directly at the anode which does not require external reforming of the fuel, which leads to highly efficient, low cost and reduced size fuel cell. The operating voltages of systems using methanol directly is 100-200 mV lower than indirect hydrocarbon systems. Methanol permeates from the anode chamber across the membrane, adsorbs onto the cathode catalyst, and reacts with air ( $\text{O}_2$ ) resulting in parasitic loss of methanol fuel and reduced cell voltage at higher current densities. Methanol and water react

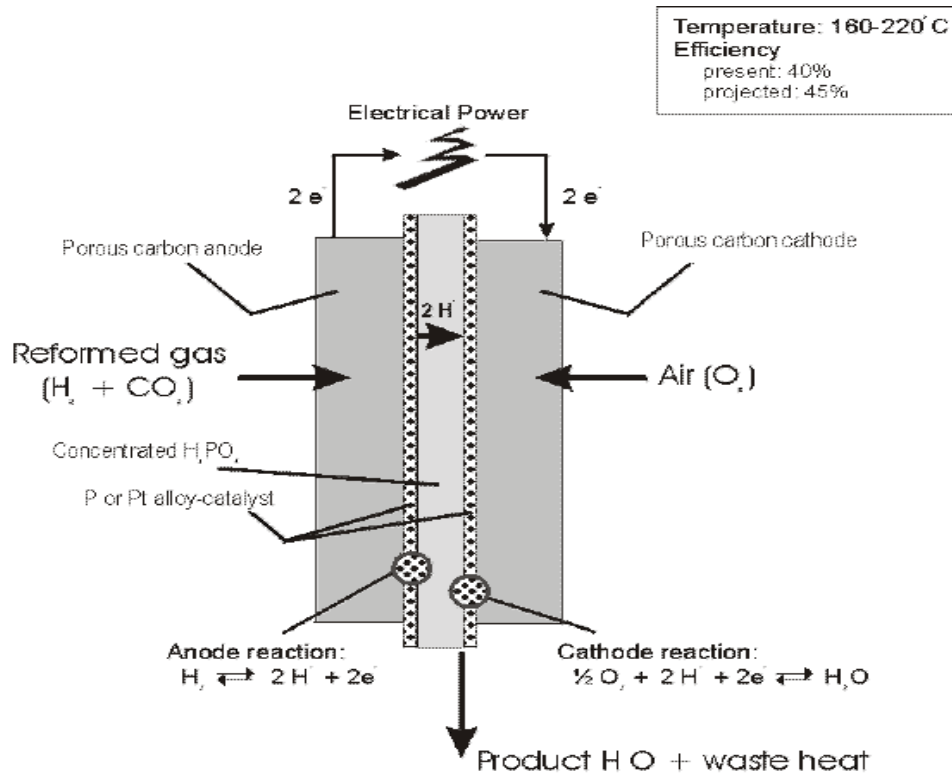
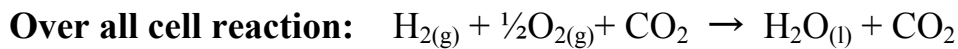
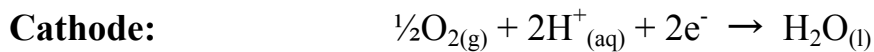
electrochemically at the anode to produce carbon dioxide, protons and electrons. The protons produced migrate through the polymer electrolyte to the cathode where they react with oxygen to produce water. These reactions are promoted by the incorporation of platinum-based electro catalyst materials in the electrodes. Methanol oxidation, which is irreversible, is a six-electron process and the product of oxidation  $\text{CO}_2$  is rejected by the electrolyte. The maximum theoretical voltage is 1.186 at  $25^\circ\text{C}$ . The potential developed is a mixed potential involving reaction of  $\text{HCHO}$  and  $\text{HCOOH}$  species.



## **Phosphoric Acid Fuel Cell (PAFC)**

The Phosphoric Acid fuel cell (PAFC) is in a mature state in terms of technological advancement. Acid fuel cells with phosphoric acid as electrolyte use relatively clean, reformed fuels (Natural gas, LPG, light distillates). Phosphoric acid has the advantages of good thermal, chemical and electrochemical stability, good capillary properties and low vapor pressures though it is a poor ionic conductor. Among the common acids, it has the lowest volatility and this property allows PAFCs to operate at 463K to 473K for several thousand hours. Other inorganic acids such as HCl, HF, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> have lower thermochemical stability and higher vapour pressures and therefore not suitable for operations at high temperatures (>473K). H<sub>3</sub>PO<sub>4</sub> is the only inorganic acid that is suggested for its utility in fuel cell applications for these reasons. The concept of employing "super acids" was discussed many times in the past, but did not progress beyond research age. The water vapor-pressure-concentration characteristics are almost ideal. It permits wide change of vapour pressure across the face of the cell and as a function of current density, without showing a tendency to dry out or become too dilute, this is in marked contrast to KOH solutions, which tend to dry out; electrolyte circulation is essential in alkaline cells. It exhibits high tolerance for reformed hydrocarbons, removal of CO is possible by a shift reaction, and CO<sub>2</sub> is rejected naturally.

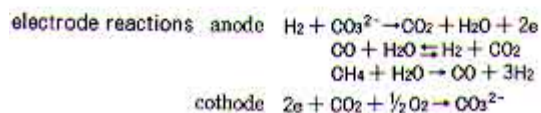
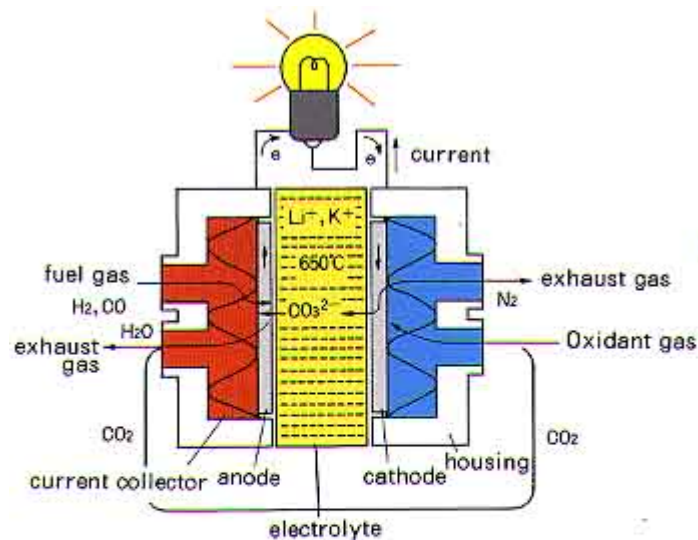
The major limitation of this acid is that oxygen reduction is very slow even at high temperatures and pressures.



Phosphoric acid with the function of the electrolyte is fixed in a porous layer between the electrodes. The advantage of this type of fuel cells is their relatively simple construction, mainly based on the use of carbon, PTFE and SiC which all can be processed by methods which are well-known from the origin of the fuel cell technology and could be easily adjusted to the demands of the fabrication of PAFC fuel cell components.

## Molten Carbonate Fuel Cell (MCFC)

Molten carbonate fuel cells are approaching the early stages of commercialization, having been under study and development for more than 40 years. The high operating temperatures of MCFCs offer the prospect of being able to internally reform fuels such as natural gas. Long start-up times are implied, expensive materials are needed, and a number of design challenges are encountered due to leakage, corrosion, and loss through vaporization of the electrolyte. One of the most promising aspects of molten carbonates is the possibility of using, apart hydrogen, low cost fuels, as methanol, gaseous carbon.  $\text{CO} + \text{H}_2$  (syngas) resulting from methane conversion by thermal cracking or reforming reaction. The oxidant is constituted by a mixture of air and carbon dioxide in the proportions of 70% and 30% respectively.

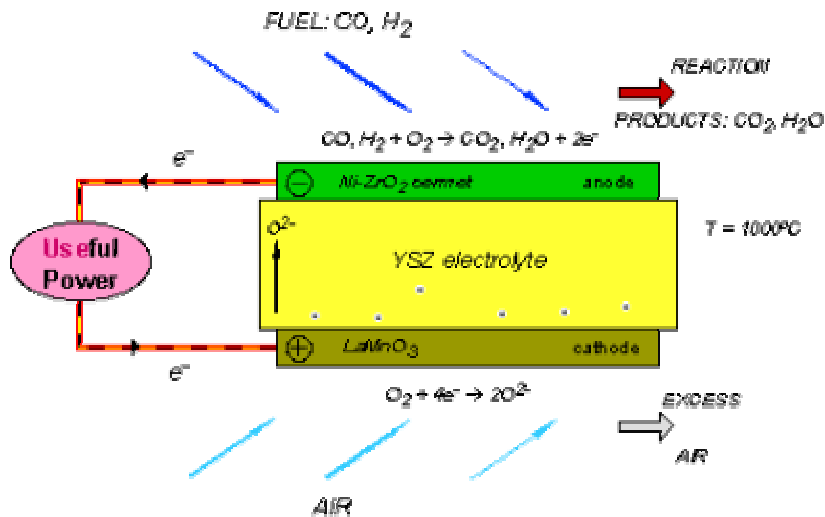


Principle of Molten Carbonate Fuel Cell.

In operating MCFC, electrons are transferred from the anode through an external circuit to a cathode, where they participate in reduction reactions. Negative charges are conducted by carbonate anions ( $\text{CO}_3^{2-}$ ) from the cathode through the molten electrolyte to an anode. At the anode, electrons are produced by oxidation. MCFCs differ in many respects from PAFCs because of their higher operating temperature and the nature of the electrolyte. The higher operating temperature of MCFCs provides the opportunity for achieving higher overall system efficiencies and greater flexibility in the use of available fuels. On the other hand, the higher operating temperature places severe demands on the corrosion stability and life of cell components, particularly in the aggressive environment of the molten carbonate electrolyte. Another difference between PAFCs and MCFCs lies in the method used for electrolyte management in the respective cells. In a PAFC, PTFE serves as a binder and wet-proofing agent to maintain the integrity of the electrode structure and to establish a stable electrolyte/gas interface in the porous electrode. The phosphoric acid is retained in a matrix of PTFE and SiC between the anode and cathode. There are no materials available for use in MCFCs that are comparable to PTFE. Therefore, a different approach is required to establish a stable electrolyte/gas interface in MCFC porous electrodes. The MCFC relies on a balance in capillary pressures to establish the electrolyte interfacial boundaries in the porous electrodes.

## Solid Oxide Fuel Cell (SOFC)

In the operation of SOFC, negative charges are conducted by electrons from the anode through an external circuit to the cathode; it is conducted by negative ions ( $O^{2-}$ ) from the cathode through the electrolyte to the anode. Its typical operating temperature is 1273 K; at this temperature, the electrolyte is an oxygen-ion conductor, and the free energies (as a consequence, the associated Nernst potential) of the overall reactions are substantially lower than at lower temperatures (e.g. 43.3 Kcal/mol at 1200 K vs 54.6 Kcal/mol at 300 K for  $H_2$ ). The heat of reaction is almost independent of temperature; therefore the potential (ideal efficiency) is reduced by the high temperature operation.



Different SOFC designs have been developed to implement the fuel cell and reformers into the stack and, ultimately, the complete system. Three main

designs are encountering rapid development in SOFC technology: tubular, planar and monolithic configurations. Tubular SOFC designs are closer to commercialization and are being produced by several companies around the world. Demonstrations of tubular SOFC technology have produced as much as 220 kW. Since SOFC requires high operating temperatures, their most common application is in large, stationary power plants. The high temperatures open the opportunity for “cogeneration”-using waste heat to generate steam for space heating, industrial processing, or in a steam turbine to make more electricity. Although they require inverters to change their direct current to alternating current, they can be manufactured in relatively small modular units. The compact size and cleanliness of SOFCs make them especially attractive for urban settings.

### **Biochemical Fuel Cells (BFC)**

Biochemical fuel cells (BFCs) are devices for converting chemical into electrical energy using a bioorganism as an intermediary or as an electrode. Either or both electrode process may be promoted by biochemical agents. The concept was extremely popular in the early 1960s when it was taken up by NASA (National Aeronautics and Space Administration, USA). NASA's interest in studying the production of electricity by means of biochemical reactions stemmed from the association with the problems of waste management in the closed system of a space shuttle during longer space flights. Therefore, algae and bacteria were among the first organisms used in this phase of experiments with biochemical fuel cells. The first experiments in the field of biochemical fuel cells were performed in 1911. It was Potter who first postulated a relationship between electrode potentials and microbial activity. Potter measured the potential difference between two



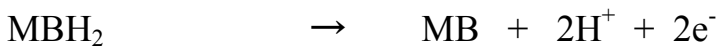
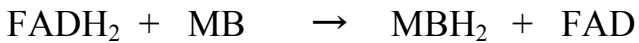
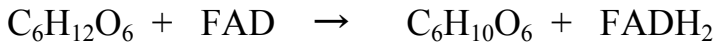
electrodes, one of which was inserted into a bacterial culture and the other into a sterile culture medium. He actually made what can be considered to be the first biochemical fuel cell battery by assembling six cells, each of which consisted of a yeast–glucose half-cell and a glucose half-cell without microorganisms. Similarly, in 1931 Cohen studied the potential differences arising between various cultures and sterile media; he also built a bacterial battery, which produced a small current for a short period of time. Cohen found that the potential of a vigorously growing bacterial culture amounted to 0.5–1 V over the control medium. The greatest deficiency of the microbial half-cell was that its current output was generally very low ( $10^{-5}$ – $10^{-6}$  A). Further progress in these devices has been made since 1959.

#### Characteristics:

1. The temperature of operation ranges from 0-40°C.
2. The cell has a pH of 7.0.
3. It has low ionic strength.
4. Raw materials like vegetable and fruit extracts, petroleum extracts and human waste, should be available in plenty. Carbonates and sulphates are generally used as oxidants.
5. Cell reactions can be photo assisted and solar energy utilization is possible.
6. Unit cell voltages are low since  $\Delta G$  for both reactions is low. So is the power output. Experimental cells have produced several watts per square centimeter.
7. Current output is low. This is due to the small ionic strength of low conductance of the dilute solutions of the bioagents in active state.

## Mechanism

A typical biochemical fuel cell mechanism at the anode is given below. The enzyme-catalyzed reaction involving glucose is a two-electron process with methylene blue (MB) acting as an intermediate.



The electrons released are utilized in the cathode reduction process. FAD is the coenzyme of glucose oxidase, and plays an important role in enzyme activity. The reaction is seen to be a four-electron process when living bacteria are used. The conversion efficiencies are low for the enzyme reaction. Both MB and FAD are regenerated.

There remain many technical difficulties in DMFC to be overcome:

- 1) Poisoning of the platinum based electro catalyst by unconverted methanol residues and these results in a decline in cell performance. To solve this problem, a much more effective co-catalyst or promoter has to be found to combine with the platinum. Finely-divided platinum-ruthenium alloys supported on carbon materials were the best catalysts for methanol electro-oxidation.

- 2) There is also the problem of methanol crossing over to the air electrode; the methanol is transferred in solution by the highly hydrated hydronium ions in the PEM electrolyte. Such cross-over decreases system efficiency, through loss of fuel into the air stream, and causes poisoning of the air electrode. It has been found that methanol cross-over is more manageable with a circulating liquid sulfuric acid electrolyte and a suitable micro porous membrane than with a solid PEM electrolyte.
- 3) Charge transfer in sulfuric acid appears to proceed via 'proton hopping' and the tortuous passage through the micro porous membrane restricts the transfer of methanol. Indirect proof of this mechanism has been provided by studies on hydrazine fuel cells (15). When using a similar liquid electrolyte membrane system, stoichiometric electrochemical conversion of hydrazine was obtained, i.e. no fuel reached the air electrode. In summary, DMFC remain much further from commercialization.

**CHAPTER 5**  
**EXPERIMENTAL, RESULTS AND DISCUSSION**

**DESIGN OF THE FUEL CELL:**

Any electrochemical cell has two electrodes and a suitable electrolyte. The design of the fuel cell has to have additionally some devices which can feed the fuel to the anode and oxygen to the cathode. In addition in order to avoid the transport of the fuel to the cathode and thereby reduce its oxygen reduction capacity is usually prevented by a membrane.

Using this basic principle, the cell has been designed in this study and the designed cell in its actual dimensions is shown in Fig.1.



Fig.1. Various components of the Fuel cell designed

The two electrode assembly is separately shown in Fig.2.

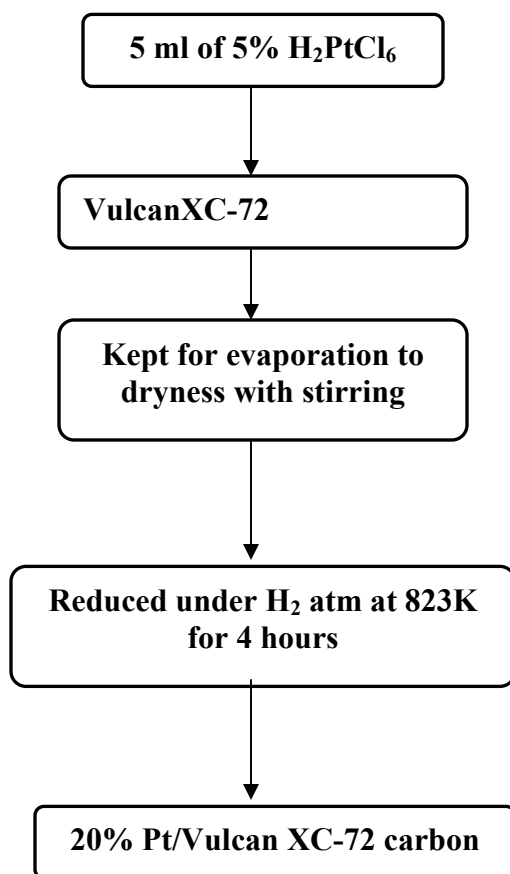


Fig.2. The electrode assembly

The electrode is Platinum supported on carbon ( 20 wt % Pt). The carbon support used, is Vulcan Carbon XC72 supplied by The Pt loading on the carbon support was carried out as shown in the following scheme.

5 ml of 5%  $\text{H}_2\text{PtCl}_6$  was added to 0.5 g of Vulcan XC-72 carbon to get 20 % Pt loading. The above mixture was kept for evaporated to dryness with stirring. The resultant material was reduced under hydrogen atmosphere at 823 K for 4 hours and it was made into the form pellet using PTFE solution as binder. Silver paint was coated on one side of the pellet to get contact between Tungsten wire and Pt loaded carbon.

## Preparation of 20% Pt / Vulcan XC-72 as electrode



Scheme.1. Procedure for preparation of the electrode

The fuel, in this case methanol is fed to the anode by carrying methanol vapours with nitrogen carrier gas and in this way flooding of the electrode is avoided. Oxygen from the cylinder is fed to the cathode. The electrical leads to the electrodes are established by using silver paint and tungsten leads are taken through glass tube as shown in Fig.

The electrode in the form of a pellet is prepared by using the platinum loaded carbon

In a pellet press applying a pressure and the process of pellet making is shown in Fig.3 and Fig.4.



Fig.3 & 4 : Pellet press used for preparing the electrode.

The cell as set up for measurement is shown in Fig.5 and Fig.6

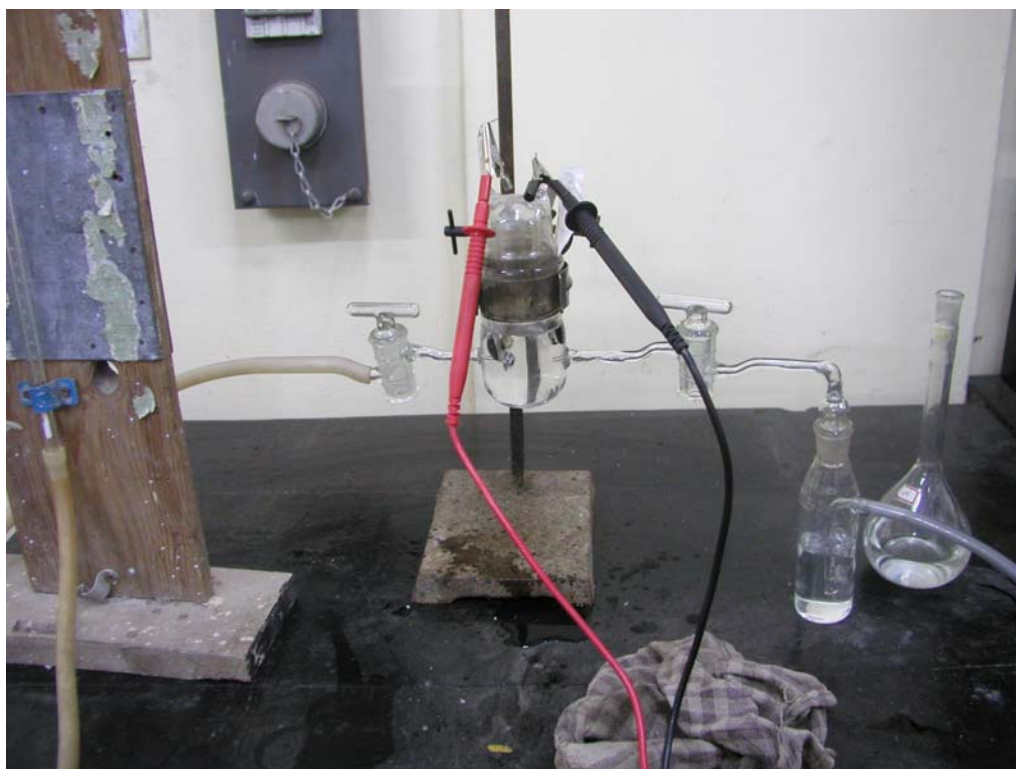


Fig.5 & 6. Working configuration of the Fuel cell



The output voltage generated is measured in a voltmeter with suitable digital accuracy and it is around 1.06V and it varies with the concentration of the electrolyte, KOH, used. However, the flow rate of Nitrogen for feeding the Methanol didn't have much effect on the voltage generated, showing that the procedure adopted was providing enough methanol at the anode. The variation in the flow rate of oxygen to the cathode also had negligible effect.



Fig.7. The measurement of voltage developed by the Fuel cell.

The use of membrane is avoided in this configuration since the cell as designed could not be provided with a membrane though it is possible to incorporate with suitable groves in the cell a membrane. In stead of the membrane the flooding of the anode was avoided by controlling the flow rate of nitrogen so that the amount of methanol fed to the electrode is

completely combusted and does not cross over to the cathode and inhibit the oxygen reduction reaction.

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