Fuel Cells - Challenges Ahead

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Introduction

Among the available options for energy conversion deices, fuel cells have been considered as one of the possibilities for a number of decades now.   However in spite of concerted and persistent efforts, still only hope is expressed without realization of any remarkable breakthrough or penetration of fuel cells in the energy market economy.   It is therefore essential that the situation is completely analyzed and the prospects and challenges are clearly delineated. This presentation makes an attempt to bring out at least some of the scientific challenges faced and the prospects of fuel cells.   In a recent publication Rand and Dell [1] have examined the virtues of hydrogen energy while pointing out the difficulties to be faced. This analysis has hence led that the concept of hydrogen economy itself is unrealistic.   They have rightly pointed out that it is not possible to reach a simple unequivocal conclusion regarding overall prospects since the international energy situation is so complex and predicting long term future is notoriously difficult. The aspects prospects and challenges of fuel cells have been considered by many others in the past [2].

Fuel cells are simple energy conversion devices where the chemical energy of the fuel is directly converted into electricity.   It is therefore possible that a variety of fuels can be considered.   Typical fuels and the respective energy density obtainable from each of them are given in Table.1.   It is seen from the data in Table 1 why hydrogen is the most preferred fuel compared to other fuels.

In addition of the available choice of the fuels, there is also a choice on the configuration of the fuel cell.   The available configurations are based on various parameters like temperature of operation, choice of the electrolyte, fuels employed and other variable experimental parameters. In Table 2, one of the specific representations is

shown for the configuration of the fuel cells.   Depending on the type of application and also the availability of fuels, the choice of the fuel cell has been made.   However in the last two decades, it has been recognized that for portable power, PEMFC (Proton Exchange Membrane Fuel Cell) has been advocated as the choice and it is generally felt

Table 1 Chemical and Electrochemical data on various fuels for choice of fuels and oxidant
(Oxidant ---- gaseous oxygen/air (In general, the oxygen needed by a fuel cell is supplied in the form of air)

FUEL	ΔG^0 kcal/mol	E^0 Theoretical (V)	E^0_{max} (V)	Energy density (kWh/kg)
Hydrogen	**-56.69**	**1.23**	**1.15**	**32.67**
Methanol	**-166.80**	**1.21**	**0.98**	**6.13**
Ammonia	-80.80	1.17	0.62	5.52
Hydrazine	-143.90	1.56	1.28	5.22
Formaldehyde	-124.70	1.35	1.15	4.82
Carbon monoxide	-61.60	1.33	1.22	2.04
Formic acid	-68.20	1.48	1.14	1.72
Methane	-195.50	1.06	0.58	-
Propane	-503.20	1.08	0.65	-

that as when the temperature of operation for Solid Oxide Fuel Cells (SOFC) can be brought down, it may be one of the preferred choice for stationary power.   However both of these systems appear to be under development stage even now though a few of the other fuel cell configurations have been employed for power generation.   Whatever may the ultimate choice of the fuel cells, the scientific challenges faced appear to be mostly common for most of the fuel cells.   The performance of a fuel cell is usually evaluated in terms of the polarization curve, which is a plot of potential as a function of current.   A typical polarization plot usually obtained is shown in Fig.1.   These plots have three characteristic regions denoted as activation, ohmic and mass transport losses indicating why the observed potential is lower than the thermodynamic reversible potential that can be realized for a particular combination of fuels and fuel cell configuration.   It will be seen that the activation losses seem to contribute substantially for the lower value of the

potential that can be realized in the fuel cell at low current densities.   This loss accounts for nearly 35-40% of the total potential that can be realized in a fuel cell.   The reduction in the realizable potential arises due to the electrochemical reaction taking place in the cell.   It is therefore necessary to identify the electrochemical reaction is taking place at the electrode/electrolyte interface and remedy it by the proper choice of the electrode,

Table 2.   Configuration and application of various fuel cells with other typical operating parameters

Fuel Cells → Low Temperature Fuel Cells, Medium Temperature Fuel Cells, High Temperature Fuel Cells

| Characteristic	PEMFC (Proton Exchange Membrane Fuel Cells)	DMFC (Direct Methanol Fuel Cells)	AFC (Alkaline Fuel Cells)	PAFC (Phosphoric Acid Fuel Cells)	SOFC (Solid Oxide Fuel Cells)	MCFC Molten Carbonate Fuel Cells)
Operating Temp (^{0}C)	60 – 80	60 – 80	100 –150	180 – 220	750 - 1050	650
Fuel	H_2 (pure or reformed)	CH_3OH	H_2	H_2 (reformed)	H_2 and CO reformed & CH4	H_2 and CO reformed & CH4
Charge carrier in the electrolyte	H+	H+	OH-	H+	CO32-	O2-
Poison	CO >10 ppm	Adsorbed intermediates (CO)	CO, CO2	CO >1% H2S >50 ppm	H2S >1ppm	H2S >0.5 ppm
Applications	Transportation, Portable		Space, military		Power generation Co-generation	
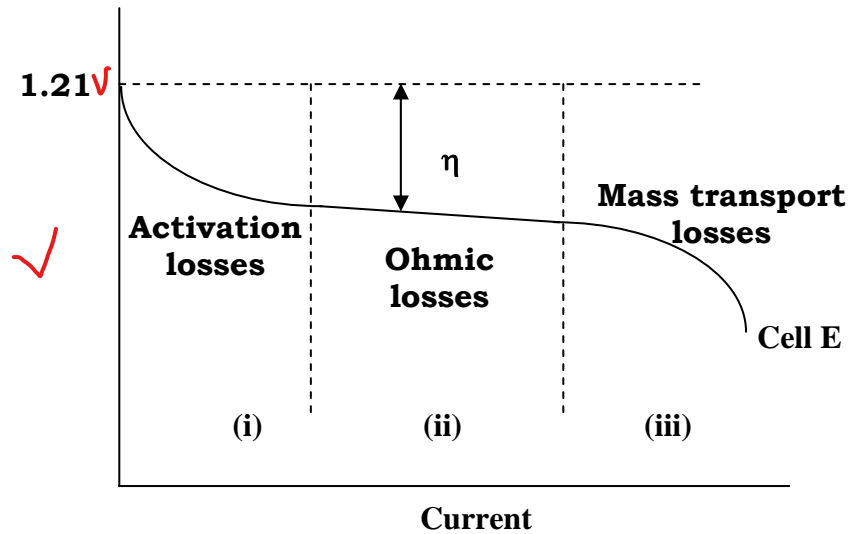
Fig.1. Typical Polarization plot obtained for a fuel cell.(note at zero current the potential is given by the reversible thermodynamic value).

In an ideal (reversible) fuel cell, the cell voltage is independent of the current drawn. However the reversible cell potential is never realized even under open circuit (zero current) conditions due to various irreversibilities that arise due to fuel cell operation. The difference between the actual realized voltage at a given current density and the reversible cell voltage for the reaction concerned is termed as over voltage (if referred to a single electrode it is usually termed as over potential).   Prominent sources of overvoltage in a fuel cell are

1. **Mixed Potential at electrodes:** This potential arises due to unavoidable parasitic reactions that tend to lower the equilibrium potential of the electrode. One of the ways of visualizing this factor could be the cross over of the fuel from anode to cathode or the oxidant from cathode to anode. This can be the dominant sources of losses at open circuit, especially in direct methanol fuel cells where fuel crossover through the electrolyte membrane is expected.   It is also to be recognized that the carry over of the constituents of the alloy catalyst employed in the anode to the cathode and thus changing the characteristic of the cathode.

In a recent communication, Wang et al [3] examined the cross over of Ru from Pt-Ru anode to the cathode and showed that a substantial (nearly 40%) loss in electrochemical activity is caused by this cross over.   This crossed over Ru from anode to cathode not only decreased the electrochemical active area of the catalyst

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in the cathode but also probably aided the Ostwald ripening of the catalyst particles in the cathode. Though it has been shown by the cross over of species from anode to cathode in this section as an example for mixed potential, it is possible that even in a single electrode the mixed potential situation can arise due to competing substrates or participation of the species in electrolyte can cause changes in the electrochemical surface area or lead to the poisoning of the active sites and other reactions taking place on the electrode. The concept of mixed potential has long been recognized, however, the exact magnitude and direction of the potential alterations have not been established. It may be necessary to know exactly what one means by mixed potential and how does it affect the equilibrium or the desired charge transfer reaction..

2. Activation losses normally arise due to the kinetics of reaction at the electrode. It is normally conceived that it is some kind of energy barrier which must be overcome in order for the electrochemical reaction to occur. The activation potential can be considered to be the extra potential required to reduce the activation energy barrier of the rate limiting step to a value such that the electrode reaction proceeds at the desired rate. In this sense, it is usually considered to be similar to the activation energy that one encounters in kinetics of chemical reactions. The electrode reaction may involve a number of steps like the adsorption of the reactants onto the surface of the electrode, electron transfer, desorption of reactants from the surface, and the activation barrier may refer to the rate limiting step in this sequence of electrode reactions.

3. Ohmic losses arise due to the resistive losses in the electrolyte and the electrode. The effect of these losses are perhaps most pronounced at intermediate current densities (100 to 500 mA/Cm) as seen from Fig.1. The gradient change for this region (the loss of potential per unit increase in current density) is considerably lower compared to the other two losses. Though it is generally believed that the ohmic losses can be minimized by proper material choice, it has been realized that it cannot be completely eliminated. Even reduction of ohmic losses appear to be marginal.

4. Mass transport losses arise due to non-reacting diffusion in the gas diffusion layer and to reacting diffusion in the electrode layers. This effect is more pronounced at high current densities (>500 mA/cm).

The combined contributions of these sources of overvoltage cause the cell output voltage to decrease with increasing current density. Though it has been identified to be three regions of losses, all the three losses can exist throughout the range of current densities and the regions are only indicative of major contribution from the particular loss identified in that region. Comprehensive discussion of the overvoltages can be found in literature [4]. Even though, we seem to recognize the various types of overvolatages, the reduction of each one of them to the minimum level appears to be difficult. Especially one is tempted to imagine that the activation overvoltage has to be associated with the electro-catalyst and optimizing the nature of the catalyst may reduce this over voltage. On this basis, various electro-catalyst formulations have been proposed for each type of fuel cells, taking into account the nature and physical state of the electrolyte, but however, it has always seen that the power out put considerably decreased since the activation losses is considerable and the drop is also steep. The formulation of the active electro-catalyst alone may not be sufficient. One has to recognize and identify the relationship and differences between activation by thermal means and application of potential. Though essentially they may be similar in activation, their effects may not be following the same mathematical formulation.

Electrode materials for fuel cells

Both noble and non-noble metal based electro-catalysts were investigated for fuel (H₂) oxidation and oxygen reduction. In the case of noble metal electrocatalysts, platinum based materials appear to be the best, whereas in the case of non-noble metal electrocatalysts several materials like metal oxides, carbides, nitrides and chalcogenides were investigated depending on the temperature of operation of fuel cell devices. The essential criteria for a better electrode material are:

• high electronic conductivity

• high adsorption capacity towards the fuel and oxygen or air

- chemical and structural stability under the conditions employed in devices i.e., operating temperature, wide range of oxygen partial pressure, concentration of electrolyte

- chemical and thermomechanical compatibility to electrolyte and interconnector materials

- high ionic conductivity

- ability to decompose the intermediate species formed during the reduction process

- tolerance to contaminants e.g., halide ions, methanol, NOx, COx, SOx

- low cost of materials

Only Platinum based materials have shown sufficient activity in the temperature range 353-373 K (essentially for PEMFC) so as to meet the power density targets set for various applications. The extent of loading of the noble metals is in the range 20-40% and the electrode layer thickness is of the order of 10 micron to reduce the transport resistance for reactants and protons.[5]. Noble metal content in the anode is 0.2 mg per cm^2 . Lower metal loading is resorted to, but lowering of the Pt loading at the anode to the level 0.05mg per cm^2 does lead to a negligible reduction in cell power density. In order to use hydrogen from reformed hydrocarbons poisoning by CO is usually observed and hence alloy catalysts (Pt-Ru, Pt-Mo) have shown better CO tolerance[6].

Electrochemical Reduction of molecular oxygen[7,8]

The electrochemical reduction of molecular oxygen is important especially for devices such as metal-air batteries, fuel cells and air cathodes in many industrial electrocatalytic processes. Oxygen reduction reaction (ORR) has been studied over the years because of its fundamental complexity, sensitivity to the electrode surface and sluggish kinetics. The sluggish kinetics of ORR under the conditions employed in electrochemical devices is due to the low partial pressure of oxygen in air, slow flow rate of oxygen (i.e., less residence time for oxygen molecules on active sites) under ambient conditions. The main disadvantage in this important electrode reaction is the value of exchange current density (j_o) in the region of 10^{-10} A cm^{-2} in acidic medium and 10^{-8} A cm^{-2} at 298 K in alkaline solution, which is lower than the j_o value of anodic reaction in the electrochemical devices. Hence the oxygen reduction reaction usually contributes considerably to the overpotential (from the equation η = RT/nF ln(j/j_o)) and therefore results in a low efficiency in the functioning of

electrochemical devices using air as oxidant [9]. Understanding and exploitation of electrocatalysis for this reaction is needed more than any other reactions in electrochemical devices.

Conventional carbon supported platinum based materials are the active, efficient, applicable and successful catalysts for oxygen reduction at the current technology stage[10]. But the formation of –OH species on the Pt electrode surface at +0.8 V vs. NHE hinder the oxygen reduction [11] In order to compensate the loss of activity, one requires higher amounts of catalyst which dramatically increases the cost. For the cost reduction of catalyst, two approaches are currently active: (1) reduction of Pt loading [10-12] and (2) exploration of non-Pt based catalysts [13-18].

Size effect of Pt nanoparticles on oxygen reduction

Monodispersed Pt nanoparticles of different sizes (2.0, to 6.0 nm) are conventionally synthesized by reduction of platinum(II)acetylacetonate with 1,2-hexadecanediol in the presence of long chain carboxylic acid and long chain alkyl amine as protecting agents. The purified Pt nanoparticles were loaded onto carbon black under ultrasonic agitation. Face-centered cubic (fcc) structure of Pt was evident from the XRD. TEM images of the as-synthesized catalysts showed uniform size and shape Pt nanoparticles on the carbon support.

Table 3. Reaction conditions, size of Pt, onset potential and ORR activity of Pt/C catalysts [7]

Reactants	Temp (°C) and time (min)	Size of Pt on C (nm)	Onset potential for oxygen reduction (mV vs. NHE)	ORR activity at +0.7 V vs. NHE (mA cm^{-2})
Pt(acac)$_2$, 1,2-hexadecane-diol, oleic acid, oleyl amine, octyl ether	290-300 30 min	2.0	+935	1.9
Pt(acac)$_2$, 1,2-hexadecane-diol, oleic acid, oleyl amine, octyl ether	290-300 60 min	3.5±0.2	+925	4.3
Pt(acac)$_2$, 1,2-hexadecane -diol, nonanoic acid, nonyl amine, diphenyl ether	250-260 30 min	4.0±0.2	+915	3.4
Pt(acac)$_2$, 1,2-hexadecane-diol, nonanoic acid, nonyl amine, diphenyl ether	250-260 60 min	6.0±0.2	+865	2.2

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The results (given in Table 3) show that the optimum size of Pt for oxygen reduction is 3-4 nm. This is due to the alteration of energy levels associated with the particle size of Pt. Similarly, the data given in Table 4 show the activity of alloy catalysts for oxygen reduction. Non Pt catalysts have also been examined for ORR activity. Venkatesara Rao and Viswanathan have utilized reverse microemulsion method (RME) for synthesizing 20 wt% Ru_xSe_y/CDX975 catalysts and showed that $Ru_1Se_{0.6}$/C catalyst had high ORR activity. The reason for the improved activity is the stabilization of Ru active sites by Se against blocking as a result of (hydr)oxide formation. The comparable ORR activity and stability of $Ru_1Se_{0.6}$/CDX975 with that of commercial Pt/C (E-TEK) catalyst makes it as an ideal cathode material for electrochemical power devices.[8]

Table 4. Metal loading, particle size, onset potential and ORR activities of carbon supported Pt/Pd alloys and commercial Pt/C catalysts [7]

Catalyst	Metal loading (wt%) Either Pt-M or Pd-M-M'	Particle size (nm)	Onset potential for oxygen reduction (mV vs. NHE)	ORR activity at +0.7 V vs NHE (mA cm^{-2})
20% Pt-Cr(1:1)/CDX975	15.3- 4.1	5.0±0.2	+990	5.2
20% Pt-Co(1:1)/CDX975	15.1- 4.5	5.0±0.2	+975	5.0
20% Pt-Fe(1:1)/CDX975	15.4 -4.4	6.5±0.1	+955	4.2
20% Pd-Co-Mo(7:2:1)/CDX975 at 700 °C	77.7:12.3:10.0	7.1	+920	4.1
20% Pd-Co-Mo(7:2:1)/CDX975 at 800 °C	78.3:12.6:9.1	9.4	+905	3.0
20% Pd-Co-Mo(7:2:1)/CDX975 at 900 °C	78.7:12.5:8.8	13.5	+865	2.6
20% Pd-Co-Au(7:2:1)/CDX975 at 700 °C	70.2:11.2:18.6	6.3	+875	3.3
20% Pd-Co-Au(7:2:1)/CDX975 at 800 °C	71.3:11.6:17.1	8.7	+905	3.9
20% Pd-Co-Au(7:2:1)/CDX975 at 900 °C	71.8:11.3:16.9	10.4	+880	2.9
Commercial 20% Pt/C (E-TEK)		3.7	+915	3.1

Membranes

The membrane of choice is often the perfluorosulphonic acid membrane under the trade name Nafion [19].All PEM fuel cells in commercial development use this membrane or one of its analogues. The details of these analogues are given elsewhere [

20].Alternate membranes for the PEMFC applications have been developed initially mainly for reasons of lowering the cost and also avoiding the use of fluorine containing compounds. However most of the membrane development studies concentrated contained sulphonic acid groups for proton conduction.. Temperature range of operation and the tolerance to CO have been the factors which led to the search for alternate membranes. In this endeavour, the studies dealing with the development of polybenzimidazole (PBI) membranes need special mention [21]. There are various attempts in the past to outline the developments for the membranes for high temperature operation [22,23] The driving force in the development of alternate membranes is to reduce the cost of the membranes (Nafion is around \$800 per m ^{2}) to \$30- 50 per m^2. However, the search and development of alternate membranes to Nafion are mainly frustrated since the characteristics of Nafion especially the ionic conductivity could not be matched in any other membranes [24].

It may not be desirable to search for alternate membranes for fuel cell applications from the point of view of ionic conductivity. The Nafion as such due to the extensive electronegative environment may be the best proton conductor. The alternate membranes sought should be stable under less humid conditions, with reduced or restricted swelling index with respect to Nafion, and should be capable of reducing the fuel cross over as compared to Nafion.

It may therefore be necessary that one has to seriously consider developing alternate cheap membranes or to bring down the cost of Naion at \$50 per m^2.

Solid Oxide Fuel cells

The Solid oxide fuel cells is a strong candidate for stationary power generation. Typical cell reactions are shown in Fig.2. Both the electrolyte and electrodes consist of ceramic materials The SOFC is normally developed in three cell configurations electrolyte-supported cells, anode supported cells and metal supported cells depending on which component is thickest and contribute to the mechanical stability. Due to the high temperature operation of these cells, matching of the thermal expansion of the cell components and interconnects to prevent cracking is an important factor of consideration. Yttria stabilized Zirconia (YSZ), Ceria doped with 10% GdO (GCO), $La_{0.9}Sr_{0.1}Gd_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) and a variety of other materials like Scandium doped
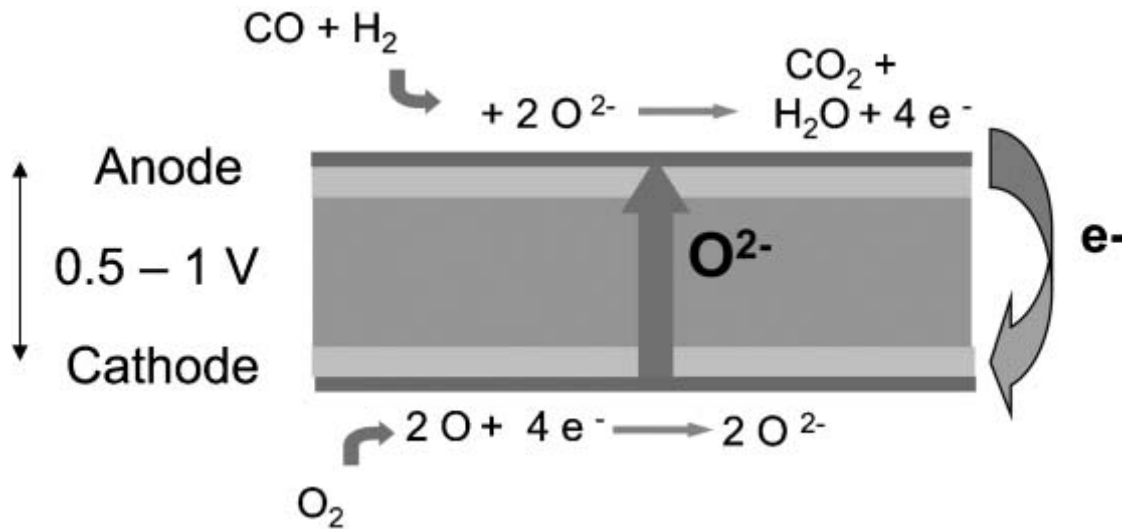
Fig.2. Basic principle of the SOFC, for the case where both hydrogen and CO are in the anode feed. [reproduced from ref26]

Zirconia have been examined as electrolyte material with the intention of reducing the temperature of operation of the fuel cell. Similar ceramic materials with metal are also examined as electrode materials and unlike in the case of other fuel cells (like PEMFC), in SOFC the electrode and electrolyte have to be manufactured in close conjunction. Two SOFC stack configurations are in development namely planar and tubular. It is generally believed that although the tubular SOFC is at present most developed, in the long term, planar SOFCs may offer a better cost effectiveness and higher power densities [25]. SOFC is usually considered for stationary power generation and hence the focus has been on increasing life time and robustness more than on increasing power density Typical data on the available power densities given in Table show that the power densities obtainable from SOFC stacks are comparable to the ones obtained with PEMFC. This is one aspect where attention may be required.

Table 4 Power densities of SOFC for stationary applications[26] .

	Power kW	Power density kW/l	conditions
Siemens Westinghouse tubular	125	0.1	Natural gas-air 1173-1273 K
General Electric Planar	1.1	0.53	Hydrogen-air,1073 K
CFCL ESC Planar	1-10	0.3	Reformate-air,1123 K

Hydrogen storage

On board storage of hydrogen has to be developed aggressively if the fuel cells have to find use in transport sector. Several storage options have been considered like liquid hydrogen, pressurized hydrogen, metal hydrides, borohydrides and storage in carbon structures. In none of these materials the storage capacity could be achieved to the limits of the primary DOE standards of 6.25wt %.[27]   It is known that these materials are capable of storing hydrogen but not to the desirable levels. This implies that some factor has been overlooked in the design of these materials for hydrogen storage applications. One of the factors that must be carefully considered is that the activating species has to be identified since this will be the primary step for storage of hydrogen. Conventionally, the metallic sites are employed for this purpose and they can be expected to dissociate and adsorb hydrogen but the migration of hydrogen from these (metallic) adsorption sites to the storage sites has to be promoted by suitable means.

Technological Challenges

For the adoption of fuel cells there are also a variety of technological challenges that have to be overcome. These can be grouped into fuel cell processor technology, system integration, and these are not considered in this presentation.

Outlook

Fuel cells continue to face major technological hurdles that may require many years of research and development before they can be overcome. In addition, implementation of fuel cells must be part of a larger shift in fuel infrastructure and efficiency standards, which will require sustained economic considerations.. Taken together, these hurdles suggest that the widespread adoption of fuel cell technology may take some time. Successful advancement of fuel cell technology will require a sustained, long-term commitment to fundamental research, commercial development, and incremental. market entry. Depending on the sector of the market (portable communications (e.g., laptop computers, cell phones); stationary (e.g., residential back-up, electric utility grid support, hospitals); and transportation (e.g., fork

lift trucks, passenger vehicles, buses)) the number and the magnitude of challenges to be addressed change and various estimates are available on this factor [28]

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