FUEL CELLS - Efficient Energy Conversion Devices

B. Viswanathan
National Centre for Catalysis Research
Indian Institute of Technology, Madras

Fuel cell is an energy conversion device which converts chemical energy into electrical energy. A fuel cell consists of an anode to which a fuel is supplied and a cathode to which an oxidant, commonly oxygen, is supplied. The oxygen needed by a fuel cell is generally supplied in the form of air. The two electrodes of a fuel cell are separated by an ion-conducting electrolyte. Depending on the input fuel and electrolyte, different chemical reactions will occur.

All fuel cells have similar basic operating principle. The input fuel is catalytically reacted (electrons removed from the fuel) in the fuel cell to create an electric current. The input fuel passes over the anode is catalytically split into electrons and ions. Oxygen passes over the cathode is reduced by the electrons which are generated at anode and passed on to the cathode by external circuit. At cathode, the ions which are formed at anode and transported to cathode, combine with the oxide ions and generate the oxidized product (See Fig.1.). If the fuel appears to be hydrogen, then water is formed. The characteristic features of various types of fuel cells are given in Table.1.

Fig. 2 shows a typical voltage-current $(E$ - I$)$ discharge curve for a fuel cell with an open-circuit voltage E_{oc}. The overpotential $\eta = (E_{oc} - E)$ reflects the resistive IR losses due to the surface reaction kinetics, the resistance to transport of the working ion, H^+ or O^{2-} between the reductant and the oxidant reactive sites, and the resistance to diffusion of the oxidant and/or reductant to the catalytic sites and their products away from these sites. At low currents, the performance of a fuel cell is dominated by kinetic losses.
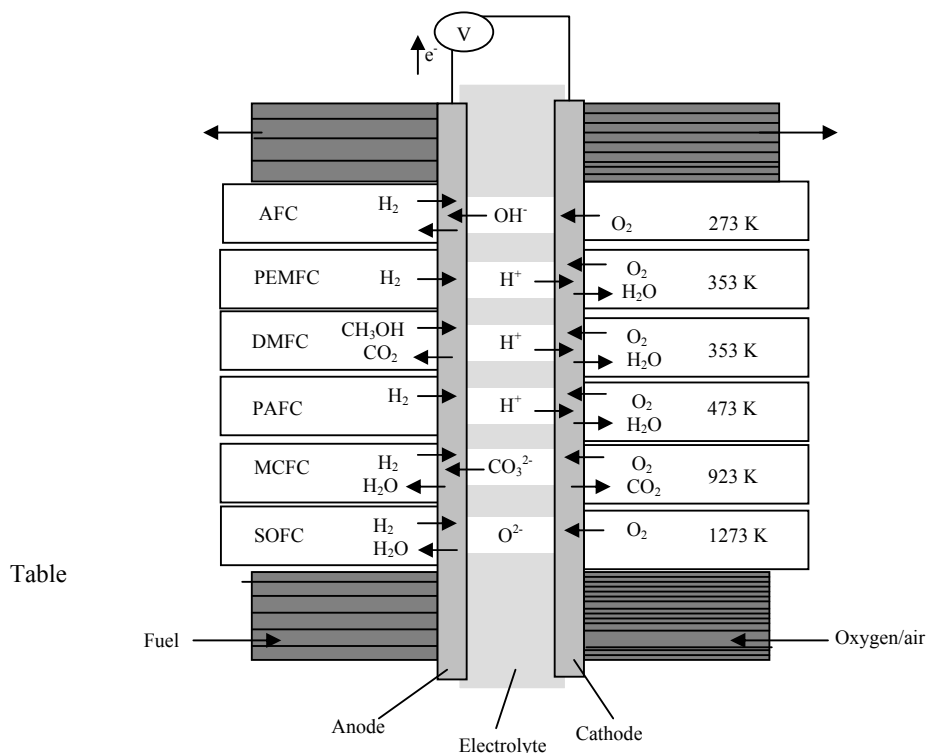

Table   6.1.

Fig. 1. Various types of fuel cells

Table 1. Characteristic features of various fuel cells

| Alkaline fuel cell (AFC)	333-423	45% KOH	OH^-	Immobilized liquid	Hydrogen	O_2/Air
Phosphoric acid fuel cell (PAFC)	453-493	H_3PO_4	H^+	,,	Hydrogen	O_2/Air
Proton exchange membrane fuel cell (PEMFC)	333-353	Ion exchange membrane (e.g., Nafion)	H^+	Solid	Hydrogen	O_2/Air
Direct methanol fuel cell (DMFC)	333-353	,,	H^+	Solid	Methanol	O_2/Air
Molten carbonate fuel cell (MCFC)	923-973	Alkali carbonate mixture	CO_3^{2-}	Immobilized liquid	Hydrogen	O_2/Air
Solid oxide fuel cell (SOFC)	1073-1273	Yttria-stabilized zirconia	O^{2-}	Solid	Hydrogen	O_2/Air
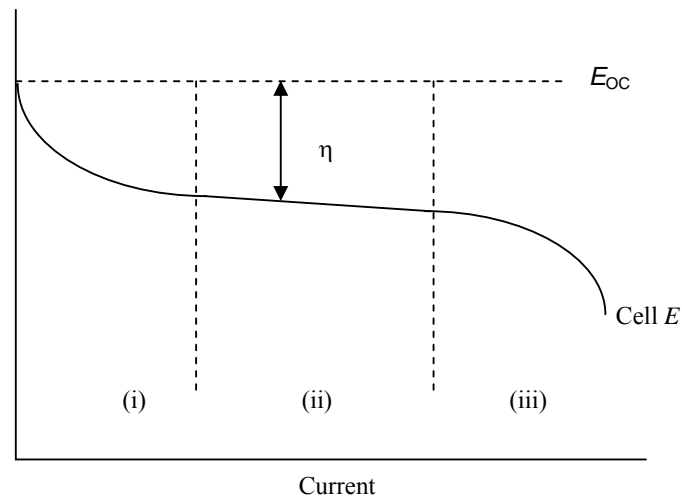
Fig. 2.. Typical polarization curve for a fuel cell: voltage drops due to: (i) surface reaction kinetics; (ii) electrolyte resistance; and (iii) reactant/product diffusion rates

These losses mainly stem from the high overpotential of the reactions occurred at anode and cathode. At intermediate currents, ohmic losses arise from ionic losses in the electrodes and separator, although contact and electronic resistances can be important under certain operating conditions. At high currents, mass transport limitations become increasingly important. These losses are due to reactants not being able to reach the electrocatalytic sites. Typically, oxygen is the problem due to flooding of the cathode by liquid water, but protons and electrons can also cause mass-transfer limitations.

At low current densities ($i_o < 1$ mA cm^{-2}), electrodes give a larger R_{tr} and therefore overpotential, η should be greater than 400 mV (at room temperature). An extremely active electrocatalyst is needed to overcome this initial voltage drop in the *E versus* current *discharge* curve

ELECTRODE MATERIALS FOR FUEL CELLS

Both noble and non-noble metal based electrocatalysts were investigated for fuel 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, NO_x, CO_x, SO_x
- low cost of materials

Electrode materials for different kinds of fuel cells have been considered.

ALKALINE FUEL CELLS (AFCS)

AFC electrodes began with Ni-based catalysts sometimes activated with platinum. Further studies with Ag and Co catalysts, Raney nickel are being undertaken in an attempt to replace some or all Pt in the electrodes. Raney nickel shows better activity for the hydrogen oxidation, but due to the wettability of the inner pores and poor chemical stability under operating conditions, decay in performance occurs. Pt/C gas diffusion electrodes are now generally used for both the anode and cathode although other possibilities are being pursued.

PHOSPHORIC ACID FUEL CELLS (PAFCS)

In the mid-1960s, the conventional porous electrodes were PTFE bonded platinum black, and the loadings were about 9 mg Pt/cm^2. During the past two decades, platinum supported on carbon black has replaced platinum black in porous PTFE-bonded electrode structures as the electrocatalyst. A dramatic reduction in platinum loading has also occurred; the loadings are currently about 0.10 mg Pt/cm^2 in the anode and about 0.50 mg Pt/cm^2 in the cathode. Alternatively, WC has been a viable electrode material for operating PAFC, because, it is resistant and stable under PAFC conditions and not contaminated by CO. Pyrolyzed macrocycles have been evaluated as oxygen-reduction electrocatalysts in PAFCs. Still Pt is favored not only due to its better catalytic properties but mainly because of the difficulties in the

production of WC and lower stability of the pyrolyzed macrocycles in hot concentrated phosphoric acid. Recently, Platinum alloys supported on carbon catalysts shown increase in specific activity over pure platinum. This translated into a 39 mV improvement in the air electrode performance at 200 mA/cm^2.

PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCS)

PEM fuel cells use a proton conducting membrane (usually Nafion 117) as an electrolyte. The catalysts are typically Pt supported on carbon with loadings of about 0.3 mg/cm^2, or, if hydrogen feed contains some amount of CO, Pt-Ru alloys are used. In order to replace Pt, several non-noble based catalytic systems like multicomponent metallic oxides, metallic glasses, metal carbides at anodic side and multicomponent metallic oxides, metal carbides, pyrolyzed macrocycles, metal chalcogenides at cathode side were exploited. Even though nanocrystallites of Pt based materials supported on carbon are currently used as anode and cathode because of the problems associated with the non-noble based materials. In DMFCs (a special case of PEMFCs where methanol is used as fuel) also carbon supported Pt-Ru at anodic side and carbon supported Pt at cathode side are the currently used.

MOLTEN CARBONATE FUEL CELLS (MCFCS)

Molten carbonate fuel cells have the electrolyte composed of a combination of alkali (Li, Na, K) carbonates, which is retained in a ceramic matrix of $LiAlO_2$. Operating temperatures are between 600 and 700 ^0C where the carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At high temperatures, noble metal catalysts are not required. Nanostructures of Ni/Al or Ni/Cr alloys have been employed as anodes. These materials are used since Ni anodes are not stable enough under operating conditions as Ni leaches out. Cathodes for MCFCs are usually NiO made by anodic oxidation of Ni or by an *in situ* oxidation of Ni metal, during the cell start-up time. Alternatives for MCFC cathodes have been found in doped lithium oxide materials such as $LiCoO_2$, $LiFeO_2$ and Li_2MnO_3, also in combination with NiO materials to form double layer electrodes. In spite of extensive research effort, lithiated NiO has remained the state-of-the-art cathode material.

SOLID OXIDE FUEL CELLS (SOFCS)

Solid oxide fuel cells employ a solid oxide material usually Y_2O_3 stabilized ZrO_2 (YSZ) as the electrolyte. Since these fuel cells also will be operated at high temperatures around 800-1000 ^0C Pt based electrode materials are not needed. Anode for SOFC is usually stabilized Ni cermets. NiO anode is slightly soluble in YSZ electrolyte. Doped cerium oxide based YSZ anodes were seen to have a higher activity and possess better ionic and electronic conductivity than a Ni based electrode. Among the catalytic systems investigated as cathodes, (La, Sr)CoO_3 (LSC) and (La, Sr)MnO_3 (LSM) meet the requirements. At present, the state-of-the-art cathode material in SOFCs is $La_{2-x}Sr_xMnO_3$ (x = 0.15-0.25).

In the past 10 years, there have been major advances in the fuel cell technology associated with nano sized noble metal based electrocatalysts. Nano materials offer unique size dependent property, a large surface to volume ratio and unusual chemical/electronic synergistic effect from ultrahigh component dispersion. For example, an increase in Pt particle size from 2 to 4 nm causes the Pt surface area to drop by half. Therefore, to achieve the maximum number of sites, the Pt particles need to be as small as possible.

Nanocrystalline materials differ greatly from the conventional materials because they have large interfacial area where the atoms appear in unsaturated coordination and have many dangling bonds. This structure must have a special influence on the properties of such materials. The abrupt termination of the crystal lattice at the surface of the nanostructures obviously differs in the bonding arrangement with that of the bulk. The surface bonding results in a localized electronic structure for the surface that is different from the bulk. The energies of these localized surface orbitals normally lie in the band gap region, thus resulting in an increase in the density of states. These states depending on their energy location are thus able to exchange charge with CB or VB of the electrode and/or electrolyte. The Fermi level also varies on decreasing the particle size. The rate of an electrochemical reaction is determined by an activation energy barrier that the charge must overcome in moving from electrolyte to electrode or vice versa. Charge transfer process (oxidation, reduction or dissolution) is facile across at electrode/electrolyte interface only when the Fermi level of the electrode matches with the redox potential of the depolarizer. The charge transfer rate in the non-equilibrium condition depends on the charge carriers (DOS) in the space charge region. The possibility of altering the valence and conduction band edge positions of the electrode will be changed by going from bulk materials to nanomaterials. As a result, the electron transfer occurs from the Fermi level of the electrode to the empty acceptor states of an oxidant in solution or vice versa from filled states of a redox species in solution to the Fermi level of the metal. Hence the initial drop in the voltage will be minimized and leads to high performance of the fuel cell.

In general, the electrocatalysts will be dispersed on suitable carbon support. The desirable properties of carbon support are high chemical as well as electrochemical stability, sufficient electrical conductance, high surface area, suitable pore-size distribution and low impurity content.

The presentation will aim to bring out the current status of this area in relation to energy conversion processes and devices.