Fuel cells: Problems and prospects[§]

A K SHUKLA*, K V RAMESH and A M KANNAN

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Abstract. In recent years, fuel cell technology has advanced significantly. Field trials on certain types of fuel cells have shown promise for electrical use. This article reviews the electrochemistry, problems and prospects of fuel cell systems.

Keywords. Fuel cells; invariant electrode-electrolyte system; energy-conversion devices; electrocatalysts.

1. Introduction

In the literature (Bagotzky and Skundin 1980; Kordesch 1978; Liebhafsky and Cairns 1968; Vielstich 1970; Bockris and Srinivasan 1969), several publications have covered the history of fuel cells. William Grove in 1839 was the first to have proclaimed the discovery of fuel cells, but the impetus in fuel cell research and development started as late as 1950. This led to the successful use of H_2-O_2 fuel cells for main on-board power supply in Apollo and Gemini spacecrafts in the sixties. However, research and development of fuel cells for terrestrial applications declined in the late sixties due to their high cost, noble-metal requirements and short life. Fuel cell activity was further revived in the early seventies and was greatly enhanced in 1973 after the energy crisis (Tilak et al 1981).

A fuel cell is an electrochemical cell which can continuously change the chemical energy of a fuel and an oxidant to electrical energy by a process involving essentially invariant electrode-electrolyte system. The difference between a fuel cell and a battery is that in the former, the fuel is continuously and externally fed to the electrode, whereas in the latter the reactants are stored within. Fuel cells produce electrical energy as long as they are supplied with a fuel and an oxidant. Fuels that can be used include H_2, CH_4, NH_3, N_2H_4 and CH_3OH or H_2-rich gas derived from oil or coal or recovered from biomass. The oxidant is generally oxygen or air; other oxidants such as halogens and H_2O_2 could also be used.

The simplest type of fuel cell, viz., a H_2-O_2 fuel cell is shown schematically in figure 1. A typical unit produces voltages of less than 1 volt and current of the order of 1 A/ft^2. A number of such cells are stacked together in series or parallel to produce sizeable outputs. A fuel cell power plant consists of three major sub-systems, viz., fuel reforming, power generating and power conditioning units. The layout of a fuel cell power plant is shown schematically in figure 2. The fuel reforming processes can be in-built in the power section itself. In the power
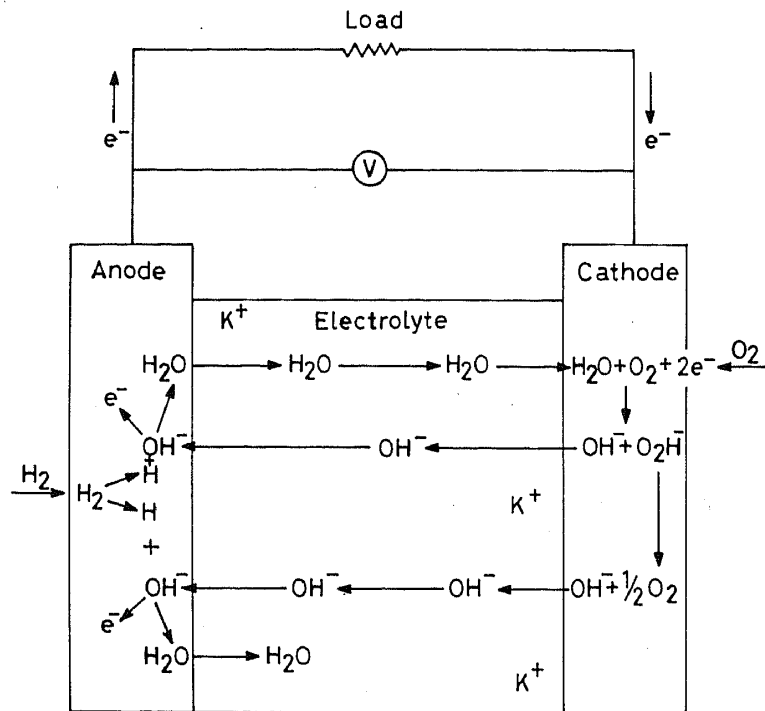

Figure 1. Electrochemical processes occurring in an alkaline H_2-O_2 fuel cell.
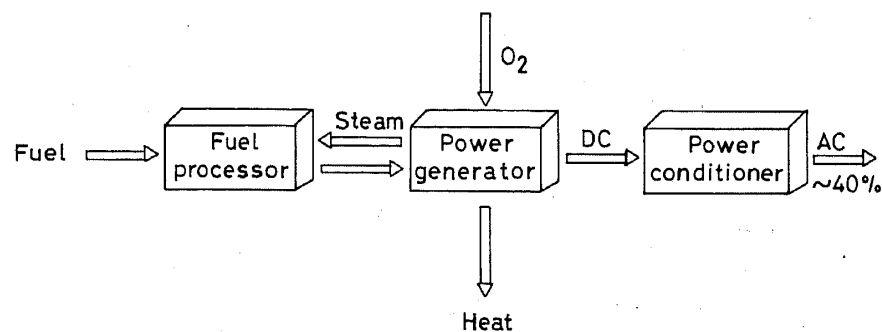

Figure 2. Fuel cell power plant.

generator, the reformate reacts with O_2 electrochemically on the electrode surfaces producing d.c. electricity and heat in the form of hot water or steam; this heat can be fed back to the fuel-reforming section.

2. Advantages of fuel cells

The efficiencies of different types of energy conversion devices are given in table 1. It can be seen that the demonstrated efficiencies of fuel cells are considerably higher in relation to other energy-conversion devices. The direct conversion of chemical energy to electrical energy in a fuel cell makes its efficiency free from Carnot's theorem. The other advantages of fuel cells include: simple, clean and quiet operation, site adaptability due to their modular nature, operation over any

Table 1. Efficiencies of direct energy conversion devices.

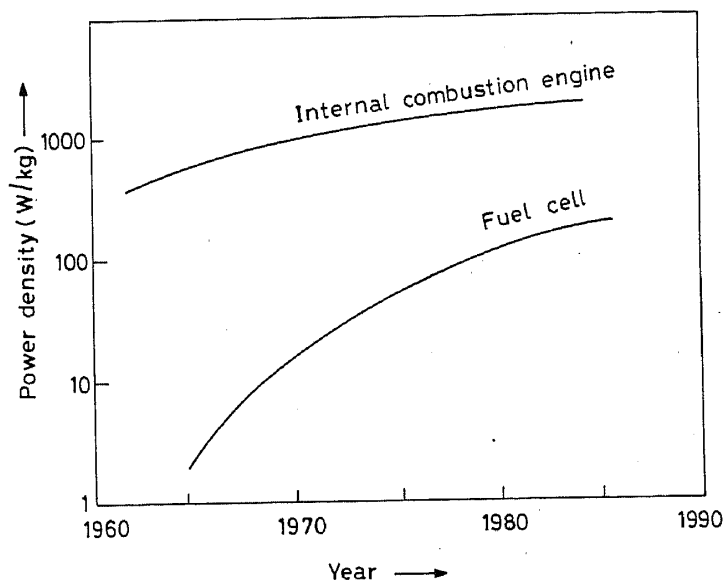| Energy converter	% efficiency
Thermoelectric	10
Thermionic	22
Photovoltaic	18
Magnetohydrodynamics	60
Low temperature fuel cells	60
High temperature fuel cells	60
Gas turbines	30
Internal combustion engines	30
Diesel engines	40

(Tilak *et al* 1981)

Figure 3. Historical trend in power densities for fuel cell and internal combustion engines.

desired temperature range and multifuel capability. Furthermore, fuel cells produce d.c. electricity which is attractive to industries that use large amounts of d.c. power, viz., chloralkali and aluminium industries. Since fuel cells feed on H_2, they are suited to industries that generate this gas as a by-product, such as the petrochemical industry. Fuel cells can be run on almost any fuel, viz., naphtha, methanol, natural gas or any H_2-rich fuel. Non-conventional fuels such as sewage-treated gases can also be used. Siting power plants close to the load keep transmission losses to a minimum and save the heavy expense of laying down transmission lines. Fossil-fuel power plants with capacities as high as 1000 MW utilize their exhaust heat to generate additional electrical energy thereby further increasing their efficiencies. Unlike coventional power sources which achieve high efficiency only when operated at full load, the efficiency of fuel cells is independent

of load. Also the efficiency of a fuel cell does not depend on its size. Only fossil-fuel plants with capacities larger than 1000 MW can approach the efficiency of a fuel cell. The modular design of fuel cells allows a utility to expand its generating capacity in small increments closely matching the needs for load following and peaking service.

Fuel cell technology has undergone substantial development (Brusaglino *et al* 1982; Shukla *et al* 1983) since 1960 (see figure 3) and it is believed that in the years to come fuel cells will become commercially feasible.

3. Types of fuel cells

Fuel cells may be generally classified as in table 2. A broad distinction between direct and regenerative fuel cells, which are similar to primary and secondary batteries, has been made. Reformer and biochemical fuel cells have been grouped under indirect fuel cells. The direct type has been further subdivided based on the temperature of operation, viz., low ($<200°C$), medium ($200–750°C$) and high ($>750°C$). The types of fuels employed in fuel cells are also indicated in the table. Fuel cells have also been grouped according to the type of electrolyte. The promising electrolytes are acids (H_3PO_4), alkali (KOH), molten carbonates (Li^+, K^+, $Na^+–CO_3^{2-}$), solid polymers (RSO_3H) and solid oxides ($ZrO_2–Y_2O_3$).

3.1 *Acid fuel cells*

In acidic fuel cells ion conduction through the electrolyte is provided by hydrogen or hydronium ions. Platinum or platinum alloys are employed as electrocatalysts with carbon (or graphite) based electrodes.

Table 2. Classification of fuel cells.

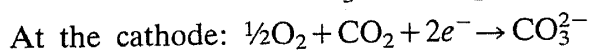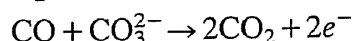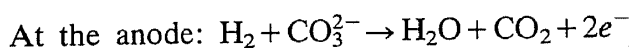|	Fuel cells				
	Direct		Indirect		Regenerative
Low temperature ($<200°C$)	Medium temperature ($200–750°C$)	High temperature ($>750°C$)	Reformer	Biochemical	
Hydrogen-oxygen	Hydrogen-oxygen	Hydrogen-oxygen	Natural gas	Glucose	Thermal
Organic compounds-oxygen	Carbon monoxide-oxygen	Carbon monoxide-oxygen	Naphtha	Carbo-hydrate	Electrical
Nitrogeneous compounds–oxygen or hydrogenperoxide	Ammonia-oxygen		Methanol Ethanol	Urea	Photo-chemical
Hydrogen-halogen Metal-oxygen or halogen			Coal Ammonia		Radio-chemical

Phosphoric acid fuel cells (PAFC) operate at 200°C. At lower temperatures, phosphoric acid is a poor ionic conductor. At higher temperatures, the problem of the stability of the carbon and the platinum catalyst arises. The advantages of PAFC are that the phosphoric acid is very stable and can be highly concentrated ($\approx 100\%$) such that the water vapour pressure is low and hence keeping the steady-state water removal by the reactant gases equal to the product water rate. Besides, at 200°C, the anode performance is good even with fuels containing carbonmonoxide upto 5%. The major disadvantage of PAFC is that the cathode, i.e., the oxygen-reducing electrode performance is poor. At present one of the objectives of R and D work on PAFC is to improve the performance of oxygen cathode. Field trials on PAFC for terrestrial applications have shown promises for commercialization (Cameron 1985).

3.2 *Alkaline fuel cells*

This is the most promising system for space applications and has been successfully used in Apollo and other space shuttles. Ion conduction in alkaline fuel cells is provided by hydroxyl ions. A wide range of electrocatalysts including nickel, silver metal oxides, spinels and noble metals can be used. The advantages of alkaline fuel cells are that the cathode performance is much superior to that in acid fuel cells and the construction materials are relatively less costly in the former cells. The main disadvantage is that the alkaline electrolytes react with carbon oxides to form carbonates which severely limit the cell performance. This necessitates scrubbing of CO_2 in the system.

3.3 *Molten carbonate fuel cells (MCFC)*

The electrolyte employed is generally a mixture of alkali-metal carbonates and the ion conduction is through the carbonate ions. Since these salts function as electrolytes only in the liquid phase, the cells operate at 600–700°C. The electrodes are made of alloys of Ir, Pt, Rh, Ni. The half-cell reactions in this cell are:

At the anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

$$CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$$

At the cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

The MCFC's have several advantages over acid fuel cells. They have high power density and higher voltages than the acid cells. Since the cell is tolerant to CO, reforming process can occur within the fuel cell and hence reformers and shift convertors are not required. Higher efficiency is achieved since the reforming process absorbs heat which is supplied *in situ* by heat produced at the electrodes of the cell. However, high temperatures impose severe constraints on materials suitability for long time operations.

3.4 *Solid-polymer fuel cells (SPFC)*

The electrolyte in these cells is an ion-exchange membrane which is impermeable to gases. Generally, cation-exchange membranes e.g. RSO_3H, are used due to their better stability and higher conductivity as compared to anion-exchange resins. The advantages of solid-polymer fuel cells are that the electrolyte being a solid cannot

Table 3. Performance of different types of fuel cells.

Types of fuel cells	Largest Unit tested (kW)	Longest stack tested (h)
Alkaline	35–60	10,000
Phosphoric acid	4,500	16,000
Molten carbonate	2	5,000
Solid polymer	5	10,000
Solid oxide	<1	5,000

change or vapourize from the system and the only liquid in the fuel cell is water; this minimizes corrosion problems. The main disadvantages are: the necessity to humidize the electrolyte; working temperatures and pressures are too low to yield good current densities and life of cells are limited due to oxidative degradation of polymers with time.

3.5 *Solid-oxide fuel cells (SOFC)*

These employ a solid, non-porous metal-oxide electrolyte with ion conduction occurring through the migration of oxide ions in the crystal lattice. Stabilized zirconia is commonly used as electrolyte and the operating temperatures of the cells are between 900°–1000°C. Solid-oxide fuel cells have distinct advantages over aqueous fuel cells as these employ no liquids and hence the problems associated with flooding of porous electrodes and maintenance of three-phase interface are totally averted. Also, the electrolyte composition remains invariant and independent of the composition of the fuel and oxidant. Since the cell operates at high temperatures, losses due to activation polarization are minimal; this avoids the use of noble-metal catalysts. In addition, these cells do not suffer from the constraints in molten carbonate cells which require recycling of CO_2 at the cathode. The main disadvantages are the high temperatures of operation and severe material limitations imposed at these temperatures. A comparison of the performance of different types of fuel cells is given in table 3 (Phadke 1985).

4. Fuel cell electrodes

One of the important components of a fuel cell is its electrodes. The main functions of electrodes are: to contain the gas/liquid/solid interface, to hold the catalyst and to serve as an electron conductor. The electrode materials must be inexpensive, structurally rigid, non-corrosive and non-reactive so that they are long lasting and electrolyte resistant.

Previously, platinum black was used as the catalyst in fuel cell electrodes. Although the electrode showed good activity, the catalyst loading was rather high. The maximum surface area that can be achieved with platinum black dispersions is about 30 m^2/g of platinum but it is rapidly reduced during cell operation due to sintering, thereby reducing fuel cell efficiencies. Effective noble-metal utilization is

obtained by dispersing the metal uniformly on a conducting support.

Porous carbon as support has proven to be most effective especially for low-temperature fuel cells. Besides being inert at temperatures upto 200°C, the electrodes can be designed with large surface area. Due to many microscopic fractures and fissures, that produce pores from 10^{-3} to 10^{-7} cm in diameter, the internal surface area of 1 cc of some of the porous carbons is around 1000 m^2. By dispersing platinum on to porous carbon supports, metal areas greater than 150 m^2/g of platinum can be achieved. Moreover, platinum-supported carbon electrodes have fairly good resistance to sintering of platinum crystallites as well as improved mass-transfer properties during cell operation.

The major disadvantage of these electrodes, however, is that flooding occurs when capillary action draws the electrolyte too far into the pores and deactivates the reaction zone. This problem can be circumvented by making the electrode hydrophobic. Polyethylene, polytetrafluoroethylene (PTFE), paraffin etc., have been used as hydrophobisizers which at the same time also act as binders for the electrodes. The structural and performance characteristics of the hydrophobic electrodes depend on the preparation technique and the mode of operation. Parameters influencing the electrode performance are the radius of the catalyst particles, the radius of the binder particles, porosities of the catalyst and binder and porosity of the support, effective electrolyte conductivity, concentration and distribution of active catalytic species, mode of impregnation of catalyst on the support, pretreatment of the electrode, gas pressure, temperature etc. (Chirkov 1975). In hydrophobic electrodes, not all the particles are wetted and it is a function of binder concentration as well as the method of fabrication. The pore structure of the electrode consists of two types of pores, viz., pores in the inner space between hydrophilic and hydrophobic layers and the pores in the hydrophobic layer with small chains of porous agglomerates of the binder. The latter factor plays a significant role. Also, the pores with radii between 25–200 Å make significant contribution to the electrochemical activity which increases with micropore volume. Successful operation of a fuel cell electrode requires the establishment of gas/electrolyte/solid interface. However, for aqueous electrolytes, there is generally no genuine three-phase junction as the pore walls on the gas side are covered with a thin liquid film. Hence, the electrochemical reaction occurs in a reaction zone of finite extension (Vielstich 1970). In actual electrodes, the pores are irregular with varying diameters and lengths.

Theoretical analysis of porous electrodes is an intricate task due to lack of precise structural details, non-linear, multi-dimensional and coupled equations and problems involved in defining the operating regions, e.g., the three phase boundaries. To overcome these complexities, an idealization of various types of pore structures has been assumed and several models have been proposed for describing operational behaviour of porous electrodes (Bartell and Shephard 1953; Giner and Hunter 1969; Chirkov 1972).

Surface area, exchange current-density, double-layer capacitance, polarization resistance etc., are some of the parameters characterizing the electrode performance which can be determined by electrochemical steady-state (Tilak *et al* 1977) and transient techniques (de Levie 1967; Rangarajan 1969; Alkire and Place 1972).

4.1 *Kinetics of fuel cell electrodes*

When an electrode is under a current load (I), its potential deviates from the reversible potential (E_r), and the total overpotential (η) at the electrode is given by

$$\eta = E - E_r = \eta_{act} + \eta_{conc} + \eta_{ohm}, \tag{1}$$

where η_{act} is the activation overpotential (arising from charge transfer); η_{conc} is the concentration overpotential (due to low concentration of reactants or high concentration of products at the electrode surface, especially at high current-densities); and η_{ohm} ($-IR_i$) is the ohmic overpotential which increases linearly with current (R_i being the internal resistance mainly comprising of the resistivities of the electrolyte and the electrode).

For a planar electrode,

$$\eta_{act} = (RT/\alpha\mathscr{F})\ln i_0 - (RT/\alpha\mathscr{F})\ln(I/A), \tag{2}$$

and

$$\eta_{conc} = (RT/n\mathscr{F})\ln(1 - I/I_L), \tag{3}$$

where i_0 is the exchange current-density (expresses equilibrium reaction rate at $I = 0$); α is the transfer coefficient ($0 < \alpha < 1$); $\mathscr{F}$ is the Faraday constant; A is the area of the electrode; and I_L is the limiting current. It is evident from (2) that the activation overpotential at an electrode can be reduced by increasing i_0 or A. Thus electrodes should have high exchange current-densities and high surface areas.

Substituting (2) and (3) in (1), rearranging and differentiating, the differential resistance is given by,

$$\frac{dE}{dI} = \frac{RT}{\alpha\mathscr{F}I} - \frac{RT}{n\mathscr{F}(I_L - I)} - R_i \tag{4}$$

Equation (4) implies that at low current-densities, the major contribution to differential resistance is from activation overpotential. As current increases, differential resistance is mainly governed by R_i linearly. When the current approaches the limiting value, the differential resistance is controlled by mass-transfer limitations resulting in the rapid decrease of the electrode potential. This description is valid only if $|\eta| \ll (RT/\mathscr{F})$. For porous gas-diffusion electrodes, however, the mathematical treatments are much more complex than (4); these are discussed in detail in several publications (Berger 1968; Bagotzky and Vasilev 1966; Breiter 1969; Srinivasan et al 1967).

4.2 *Electrocatalysis of fuel cell electrodes*

Low temperature fuel cells, which operate at temperatures below 100°C, require an adequate catalytic activity of electrode materials. The electrocatalyst should have high exchange current density and/or low Tafel-slopes. By an appropriate choice of an electrocatalyst, a particular electrode reaction can be accelerated by minimizing the overpotential. It is found that electrocatalysts are almost always based on transition metals or ions irrespective of their being present as metals, alloys, semiconductors (oxides in particular), and complexes (metal phthalocyanines and

porphyrins). This is because of the unpaired d-electrons and unfilled d-orbitals present in them which facilitate bond-formation with adsorbates. The free energy of adsorption will depend strongly on the number of unpaired d-electrons per metal atom and also on their energy levels, which in turn depend on the nature of the transition metal and its chemical environment. The chemical environment around the transition metal ion affects the properties of the metal-absorbate bond. Since electrocatalytic reactions involve both formation and cleavage of metal-absorbate bonds, most effective electrocatalysis is observed when the bond is of intermediate strength; weak bonding leads to insufficient coverage by adsorbate for it to be an effective catalyst, while a high free energy of adsorption will cause the rate of the cleavage step to be slow. This dependence on the rate of hydrogen evolution reaction is discussed in the form of a volcano curve by Parsons (1958).

An alternative method of achieving effective catalysis is to change the properties of the catalyst itself during the reaction sequence leading to the weakening of the metal-adsorbate bond, such as change in oxidation state etc. In addition, geometric arrangement of the catalyst centres also affects the catalytic activity especially for concerted reactions and adsorption of large molecules involving more than one catalytic site. Further, since large surface area of the catalyst increases the rate of adsorption of reactants, the catalyst surface is deliberately roughened to increase the current-density at an electrode. Generally, expensive electrocatalysts such as platinum are dispersed on a high surface area substrate. The substrate must be a good electronic conductor, inexpensive and corrosion-resistant to the electrolyte. Carbon is a suitable substrate for this purpose. It is found that the origin and pretreatment of carbon substrates control the activity of an electrocatalyst. Further, it is desirable that the catalyst structure be highly disordered to achieve higher activity. The presence of grain boundaries, lattice defects, kinks, screw dislocations etc., is important. However, the development of electrocatalysts as of today has been essentially empirical. Characterization studies for the surface structure of electrodes and the electrode-electrolyte interface (both *ex-situ* and *in situ*) are desirable (Sherwood 1985; Kinoshita and Stonehart 1977). There are several publications which review electrocatalysis in detail (Appleby 1974; Stonehart and Ross 1975; McNicol 1978; Fickett 1977; Fletcher 1984). Generally, noble-metal catalysts are supported on high-surface area substrates to achieve maximum utility of the catalyst and higher electrochemical reaction rates. Carbon as a substrate has many attractive properties, such as chemical stability, high surface area, electrical conductivity and both macroscopic and microscopic porosities (Appleby 1983). A wide variety of carbon substrates (Hillenbrand and Lacksonen 1965; McBreen *et al* 1981) have been employed both as electrocatalyst supports and as electrocatalysts for oxygen reduction. It is reported (Nicolau *et al* 1959; Hillenbrand and Lacksonen 1965; Ross *et al* 1974) that the surface oxides on carbon as well as the catalyst-support interactions exercise a considerable influence on the catalytic activity of the electrodes. Recently an ashless coconut-shell carbon has been reported (Manoharan and Shukla 1983; Manoharan *et al* 1984; Manoharan and Shukla 1984; Shukla *et al* 1985; Goodenough *et al* 1985; Ramesh and Shukla 1985; Ramesh 1986) to be an excellent substrate for hydrogen oxidation and oxygen reduction in fuel cells.

Other than carbon, boron carbide, tantalum boride and silicides of tungsten and titanium have been used as supports for electrocatalysts in acidic environments

(Grubb and Mckee 1966). These materials are corrosion resistant and possess high electrical conductivity. Pervoskites such as $La_xSr_{1-x}CoO_3$ and $AB'_{0.5}B''_{0.5}O_3$ (where $A = Li, Cs, Ca, Ba, Sr, La$ etc. and $B' = V, Cr, Mn, Fe, Co, Ni, Ru$ etc. and $B'' = Ti, Zr, Sn, V, Nb, Ta$ etc.) as well as certain ruthenates e.g. $Pb_2Ru_2O_7$ have also been investigated as substrates (McHardy and Stonehart 1975). The conductivity of these oxide materials is increased by incorporation of certain dopants but these are not sufficiently acid resistant. If the electronic conductivities and the corrosion resistances of these materials are improved, these could offer an alternative to carbon.

4.3. *Hydrogen oxidation electrodes*

The mechanism of the hydrogen-ionization reaction has been studied in detail in view of the revived interest in fuel cells (Breiter 1969; Appleby 1974; McNicol 1978). In acid electrolytes, the hydrogen reaction is given by

$$H_{ad} + H_2O \rightleftharpoons H_3O^+ + e^-, \tag{5}$$
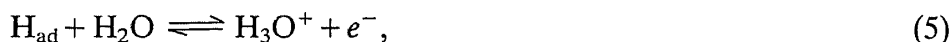
and in alkaline solution by

$$H_{ad} + OH^- \rightleftharpoons H_2O + e^- \tag{6}$$

Partial reaction steps of (5) are given by:
(a) transport of molecular hydrogen to and adsorption on the electrode surface either from the gas phase or from the electrolyte:

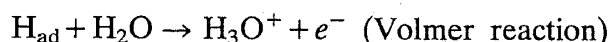$$H_2 \text{ or } H_{2_{(dissolved)}} \rightarrow H_{2_{ad}},$$

and (b) hydration and ionization of the adsorbed hydrogen which may proceed by two alternative reaction paths:

(1) dissociation of the molecules into atoms

$$H_{2_{ad}} \rightarrow H_{ad} + H_{ad} \text{ (Tafel reaction)},$$
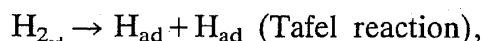
followed by hydration and ionization at discrete sites on the electrode surface.

$$H_{ad} + H_2O \rightarrow H_3O^+ + e^- \text{ (Volmer reaction)}$$

(ii) hydration and partial ionization (Heyrovsky–Volmer mechanism)

$$H_{2_{ad}} + H_2O \rightarrow [H_{ad} \ H_3O^+] + e^-$$
$$\rightarrow H_{ad} + H_3O^+ + e^-,$$
$$H_{ad} + H_2O \rightarrow H_3O^+ + e^-.$$
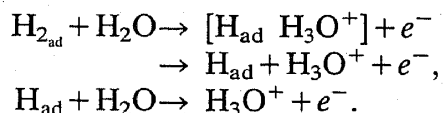
Partial reaction steps in alkaline solution can also be written in a similar manner.

Studies on anodic oxidation of hydrogen on platinum in phosphoric acid have shown that dual-site dissociation of hydrogen on platinum is the rate-determining step (McNicol 1978). The reaction mechanisms on smooth platinum, unsupported platinum and platinum supported on carbon are the same. However, the rate of the reaction is dependent on the roughness factor. In the presence of CO or S, the rate of hydrogen oxidation decreases due to the preferential adsorption of carbon monoxide on the electrode surface. In porous electrodes, diffusion processes in the pores must also be considered. At ambient temperatures, the rate-determining step is the diffusion of gas molecules through a thin liquid layer. Chemisorption of

anions hinder adsorption of hydrogen on the electrode. Hydrogen oxidation in strong alkaline electrolytes is hindered by adsorption of OH^- ions.

Only metals capable of chemisorbing hydrogen are suitable for establishment of the reversible hydrogen potentials, VIII-group metals with partially filled d-orbitals meet this requirement. At room temperature, platinum metals, especially in finely divided form such as platinum black, will establish the reversible hydrogen potential over the entire pH range, and Raney nickel will do so in alkaline electrolytes.

A large number of phosphides, arsenides, selenides and tellurides of Fe, Co and Ni have been investigated as electrocatalysts for hydrogen oxidation in sulphuric acid at temperatures less than 100°C (Mund *et al* 1973; Luft *et al* 1974). Of these, CoP_3 is the most promising and is also less prone to CO poisoning. Tungsten carbide has also been found to be an effective electrocatalyst besides being tolerant to CO poisoning (Bohm and Pohl 1968; Von Benda *et al* 1972). However, the rate constant for hydrogen oxidation on this material is two orders of magnitude lower than for Pt metal. The highest exchange-current densities of 10^{-3} A/cm^2 are obtained for the platinum-group metals. At present, the best electrocatalyst in acid electrolytes remains to be platinum dispersed on carbon with an acceptable loading of 0·25 mg/cm^2 (Cameron 1985).

Although Raney nickel is unstable in alkaline media, Ti-and Cr-containing Raney nickels (Mund *et al* 1977; Kenjo 1985) have been reported to possess higher catalytic activity and stability. The higher activity is attributed to increased d-band vacancy caused by the addition of Ti or Cr to Raney nickel. Nickel boride also exhibits moderate activity (Jasinski 1965) in alkaline electrolytes. Recently, Ta_5Si_3, Tb_4O_7 and $3Y_2O_3.2ZrO_2$ have been investigated as catalysts for hydrogen oxidation in acid electrolytes. Of these, $3Y_3O_3.2ZrO_2$ exhibits the highest activity (Tanase *et al* 1982). Noble-metal alloys such as Pt-Pd and Pt-Ru (Niedrach *et al* 1967; Stonehart 1982) have also been employed as electrocatalysts for hydrogen anodes. Pt-Ru containing carbon electrodes have been reported to possess higher catalytic activity than Pt both for hydrogen oxidation as well as oxygen reduction. Characterization studies of these electrodes reveal that the presence of Ru eliminates the formation of surface platinum oxides, thereby enhancing their activity (Ramesh 1986).

4.3 *Methanol-oxidation electrodes*

The direct methanol-air fuel cell enjoys a number of unique advantages as compared to other power generators and to other fuel cells. The challenge facing the development of a commercially viable methanol cell is to obtain adequate current/voltage characteristics. Attempts to build commercially viable, direct methanol fuel cells have encountered problems mainly concerned with inadequate anode activity. In addition, performance has been affected by electrode deterioration, possibly arising from the accumulation of the decomposition products of methanol. In order to improve the efficiency of the anode, it is necessary to examine not only the specific activity of the catalyst, but also a number of other parameters affecting electrode performance. In particular, the electrode substrate affects the rate of mass transfer of reactants and products to and from the catalytic sites. In spite of extensive research on non-noble catalysts, platinum metals still

happen to be the only useful catalyst for methanol electrodes operating below 80°C.

In acidic media, methanol could be oxidized at the Pt electrode to carbon dioxide and water, while in alkaline media the main oxidation product is the formate ion. The mechanism of methanol oxidation in these media is as follows.

(a) *In acid medium*: $CH_3OH \rightarrow CH_3OH_{ad} \rightarrow CH_2O_{ad} \rightarrow HCOOH_{ad} \rightarrow CO_2$,

    In alkaline medium: $CH_3OH \rightarrow CH_2O \rightarrow HCOO^- \rightarrow CO_3^{2-}$.

Systems using acid electrolytes have the advantage of spontaneous carbon dioxide removal but at the same time acid electrolytes are corrosive and the air electrodes in acid media perform poorly. As already indicated, alkaline systems exhibit less material problems and the use of carbon supports and silver catalysts make them cost effective.

A major improvement in electrode performance has been achieved with bifunctional catalysts. It is believed that one component of the catalyst facilitates the adsorption of methanol and the second provides an active oxygen. However, the performance of catalysts has depended to a very marked degree on the interaction of the two components both with each other and with the substrate. In the light of this fact, platinum group bi-metal catalysts, viz., Pt-Ru, Pt-Pd and Pd-Ru have been found to be more effective than the individual platinum-group metals (Binder *et al* 1972; McNicol *et al* 1976; Shropshire 1965).

4.4 *Oxygen-reducing electrodes*

Owing to the complexity of reaction and difficulties in the formation and breaking of the O–O bond, the kinetics of oxygen reduction is poor with almost all electrode materials. Oxygen reduction at the electrodes proceeds by the following pathways (Yeager 1976; Tarasevich *et al* 1983; Hoare 1968).

(a) Direct 4-electron pathway: In alkaline solutions, oxygen is reduced to OH^- through

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-,$$ the reaction potential being 0·401 V vs NHE at 25°C.

In acid solutions, oxygen is reduced to water

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O,$$ the reaction potential being 1·229 V vs NHE at 25°C.

(b) Peroxide pathway: In alkaline solutions, oxygen is first reduced to peroxide

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-,$$ the reaction potential being $-0·065$ V vs NHE at 25°C.

It is subsequently reduced through

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-,$$ the reaction potential being 0·867 V vs NHE at 25°C.

Or the decomposition through,
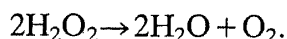
$$2HO_2^- \rightarrow 2OH^- + O_2.$$

In acid solutions, oxygen is first reduced to peroxide,

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2,$$ the reaction potential being 0·67 V vs NHE at 25°C.

This is followed,

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O,$$ the reaction potential being 1·77 V vs NHE at 25°C.

The peroxide may as well undergo decomposition as follows,

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Oxygen reduction on most of the carbon substrates proceeds mainly through the peroxide pathway (Fischer and Heitbaum 1980). Consequently, the electrode potentials correspond to 2-electron reduction of oxygen resulting in large overpotentials at open circuits itself. Incorporation of additional catalyst which promotes the peroxide elimination is therefore necessary. Rotating-ring-disc electrode (RRDE) studies on platinum and platinum alloys indicate that oxygen reduction on these materials proceeds by both direct 4-electron and peroxide pathways with the former being predominant (Tarasevich *et al* 1983; Fischer and Heitbaum 1980; O'Grady *et al* 1982). Generally, oxygen reduction kinetics is faster in alkaline electrolytes than in acid media.

Noble metals and their alloys (Peuckert *et al* 1986; Ramesh 1986; Yeager 1982; Manoharan 1984) metal oxides (Garcia *et al* 1980; Matsumura and Sato 1980; Manoharan and Shukla 1984, 1985) transition-metal macrocycles, viz., metal phthalocyanins and porphyrins (Yeager 1981; Van Veen and Van Baar 1982; Shukla *et al* 1985a; Goodenough *et al* 1985) have been studied as oxygen-reducing catalysts. Further, it is reported that heat treatment of metal-macrocycles adsorbed on carbon enhances their catalytic activity but they lack long term stability. Different oxides with spinel, perovskite and pyrochlore structures have also been reported to exhibit high catalytic activity towards oxygen reduction (Trasatti 1981; Horowitz *et al* 1983; Manoharan and Shukla 1985; Goodenough *et al* 1985; Yeager 1982). Activated carbon itself is a good catalyst for oxygen reduction in alkaline media. Various kinds of carbon have been studied as oxygen-reducing electrodes. Coconut-shell carbon reportedly reduces di-oxygen to water without peroxide formation. At present, platinum dispersed on carbon with Pt loadings of 0·5 mg/cm^2 remains the most practical catalyst (Fletcher 1984).

5. Conclusion

Fuel cell development is yet in its infancy. Like the internal combustion engines, at the end of the 19th century, there is both optimism and pessimism about their commercial potential. Stationary fuel cell power plants have a better chance of succeeding than mobile vehicular fuel cells mainly on the basis of the maximum cost/kW which the consumer can afford.

The life of alkaline H_2–O_2 fuel cells has to be improved and the costs reduced ten-fold. The cost of PAFC's has to be reduced by 50%; power densities need to be increased together with proven life. Although the efficiency and other performance

characteristics of MCFC's are satisfactory, their power sections can be quantified and made available for utility purposes only after efficient coal-gasifier facilities are available. A ten-fold increase in stack life and stack size of MCFC's is needed. It is expected that within ten years MCFC's will be competing with the advanced PAFC's especially for larger utility purposes. Solid-oxide fuel cells and their stack progress are excellent. However, fabrication techniques have to be improved to ensure reproducibility when large number of cell stacks are produced.

In the case of solid-polymer fuel cells, factors such as development of the humidification process, CO_x tolerance, cost reduction have to be optimized. One of the greatest problems in the area of catalysts for fuel cells with acid electrolytes continues to be the development of low-cost catalysts for oxygen-reducing electrodes. The catalyst should at least display an activity equal to platinum and preferably give potentials close to the well known four-electron oxygen reduction. Development of catalysts till now has been purely empirical; surface characterization studies, both *ex situ* as well as *in situ*, on electrodes could be useful in identifying the active catalytic species. It is believed that with continued world-wide efforts in appropriate areas of research, both in the scientific and engineering aspects, fuel cells would become feasible for power generation and other utilities.

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