

CHAPTER I

GENERAL INTRODUCTION

SECTION 1-1 : ELECTROCHEMICAL PROCESSES AT NOBLE  
METALS INVOLVING FUEL CELLS

A. The Basic Fuel Cell Components :

A fuel cell is an electrochemical device in which chemical energy of a conventional fuel is converted directly into electrical energy. The device has an anode at which a fuel is oxidised and a cathode at which oxygen is reduced. In a simple fuel cell hydrogen is supplied at the anode where it interacts with oxide ion to form  $H_2O$  and releases electrons to the external circuit. The electrons do work on the way to the cathode where they are captured by oxygen which is being supplied at the cathode. The oxide ions thus formed complete the circuit flowing through the electrolyte to the anode.

There are four fundamental components of any fuel cell. These are fuels, catalysts, electrodes and electrolyte.

Fuels :

The fuels may be in gaseous, liquid, or solid state. Gaseous fuels are hydrogen, hydrocarbons, reformed natural gas<sup>1</sup> and converted fuels which are made by chemically modifying a conventional fuel such as coal. Hydrogen is the simplest and most reactive fuel. Methanol<sup>2</sup>, hydrazine<sup>3</sup>, formic acid<sup>4</sup> are examples of liquid fuels used to construct fuel cells. Solids such as zinc, magnesium, and aluminium serving as fuels have

also been studied<sup>5</sup>. Coal and hydrocarbons can, however, be sources of converted fuels which can be suitably used in fuel cells.

#### Electrodes :

Fuel cell systems that involve the use of gases require porous electrodes to permit the gases in question to diffuse through the electrodes to the sites of the electrochemical reactions. The porous electrode is usually made of carbon. The electrode must be coated with catalysts with large electrochemically active area, and it must also be inert towards the electrolyte. With the understanding of the theory of porous electrodes much improved electrodes have been developed<sup>6</sup>. Carbon can be used in acid and alkaline electrolyte and with such corrosive gases as chlorine and ammonia. Metals such as nickel and silver can be employed to prepare porous electrodes to be used in alkaline medium, and tantalum and titanium with acid electrolytes<sup>7</sup>.

When the liquid fuels such as methanol, formic acid or hydrazine are employed in fuel cell, it is mixed with the electrolyte and the fuel-electrolyte solution is allowed to flow to the anode which is usually porous carbon or nickel plaque carrying the suitable catalyst.

#### Catalysts :

Electrodes of fuel cell are usually impregnated with a catalyst. The primary aim of a catalyst in the electrochemical reaction, known as electrocatalyst<sup>8</sup>, is to increase the rate of

electrochemical reactions to the point where mass transport becomes rate controlling while the overpotentials remain negligible. Electrocatalyst may be described as a substance which gives better performance that may mean greater power per unit area, higher current density or lower overvoltage. In the presence of the electrocatalyst, redox mechanisms may follow such an alternative path for the electrochemical process so as to the electrocatalyst reduces overvoltage, consequently speed of the electrochemical process as a whole increases. The electrocatalyst can play a dual role in fuel cell electrode reactions; it can enhance the rate of the reaction if chemical kinetics is rate controlling and secondly, it can influence the potential of the cell by minimising the free energy loss due to chemisorption. As in the case of heterogeneous catalysis, adsorption and desorption play an important role in electrocatalysis. Parsons<sup>9</sup> showed theoretically that in electrolytic hydrogen evolution, the exchange current, a measure of catalytic activity, is higher for metals having lower free energies for atomic hydrogen adsorption. As  $\Delta F_{ad}^0$  approaches zero the exchange current reaches a maximum. For metals having large negative heats, i.e., strong adsorbers, the exchange current decreases with  $\Delta F_{ad}^0$ . The magnitude of this effect is different for different reaction mechanisms. It must be noted that the rate-determining step for slow reactions at non-equilibrium conditions may be quite different from that at the reversible potential. The strength of adsorption bond depends on electronic factors such as work function and per cent d band character.

It also depends to some extent on the presence or absence of defects on the surface. The influence of geometric factors depends on the structural aspects and also on the presence of defects in the electrode.

Electrocatalysis acts as heterogeneous catalysis in charge transfer reactions occurring at an electrode-electrolyte interface. The rates of these reactions are influenced not only by the nature of substrate but also by the presence of an electric field across the electrode-electrolyte interface and by the nature of the electrolyte.

#### Electrolytes :

The selection of the electrolyte depends on a number of factors, such as operating temperature, removal of oxidised product, conductivity of the electrolyte, corrosive action to electrodes or the cell materials etc. Sulphuric acid, alkali metal hydroxide and phosphoric acid are the usual electrolytes used in fuel cells.

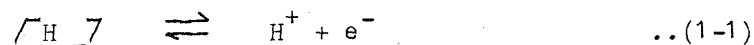
#### B. Electrode Kinetics :

It is usually found that the terminal voltage of a cell is less than the reversible potential and as current is drawn from the cell, the cell voltage decreases. The loss of voltage is due to the polarisation of the electrodes. There are three principal types of polarisations, namely ohmic; activation and concentration. The ohmic voltage loss arises

because a voltage gradient is necessary to drive charged ions through the electrolyte or electrons through the electrode material. The term 'concentration polarisation' refers to reaction control by mass transfer. If a reactant is removed rapidly by electrochemical reaction, there will be a concentration gradient set up. The driving force for mass transfer will be this concentration gradient. The electrode will be then concentration polarised. The term 'activation polarisation' is applied to the voltage loss that occurs when reactions of high activation energy - charge transfer, adsorption, surface reaction are slow.

The kinetics of electron transfer :

Let us consider the simple reaction



that takes place at the electrode surface. The potential energies of the system can be represented in Fig. 1-1-1.  $\Delta F_1^*$  is the standard state free energy of activation for adsorbed hydrogen atom,  $\text{M(H)}$ , going to the transition state. Similarly,  $\Delta F_2^*$  is the standard state free energy of activation of hydrogen ion, approaching the electrode surface to form the transition state and  $\Delta F^0$  is the chemical standard - state free energy change of  $\text{[H]} \longrightarrow \text{H}^+ + \text{e}^-$ ,

$$\Delta F^0 = \Delta F_1^* - \Delta F_2^* \quad \dots(1-2)$$

Curve 'a' represents the potential energy of the  $\text{H}^+$  and the separate electron (The effect of the electrical potential on the activation energy is shown by the curve 'b' ). If a potential difference  $\psi$  between the solution and the electrode surface,

is impressed across the system, potential energy of the system is increased by  $nF(-\psi_1)$  [  $n$  is the algebraic charge on the ion ] shown by the curve 'b'.  $\psi_1$  is measured from the electrolyte to the electrode,  $-\psi_1$ , is the voltage increase at the plane of closest approach over that when no double layer is present.

So in the presence of the impressed potential  $-\psi_1$ ,

$\Delta F_1^* + \alpha nF(-\psi_1)$  is now the free energy of activation for  $M(H)$  going over to the transition state and

$\Delta F_1^* - \Delta F^0 - (1 - \alpha) nF(-\psi_1)$  for the reverse process.

The value of  $\alpha$  depends on the relative slopes of the potential energy curves at the point of interaction<sup>9</sup>,  $\alpha$  is usually referred to as the transfer coefficient. The rate of the forward reaction (anodic) will be given by

$$v_f = \left( \frac{k_b T S}{h \gamma^*} \right) (H) \exp \left( \frac{-\Delta F_1^*}{RT} \right) \exp \left( \frac{\alpha n F \psi_1}{RT} \right) \quad \dots(1-3)$$

and that for the reverse reaction

$$v_b = \left( \frac{k_b T S}{h \gamma^*} \right) (M)(H^+) \exp \left[ \frac{-(\Delta F_1^* - \Delta F^0)}{RT} \right] \exp \left[ \frac{-(1-\alpha)nF\psi_1}{RT} \right] \quad \dots(1-4)$$

where  $n = 1$  in this case.  $(H)$ ,  $(M)$ ,  $(H^+)$  are the activities of the species,  $k_b$ ,  $h$  are Boltzmann's constant and Plank's constant.  $S$  is surface concentration (g.moles/cm<sup>2</sup>), such that  $\gamma H/S = (H)$ ,  $\gamma$  is activity coefficient and  $H^* = S(H)^* / \gamma^*$ .

For a general electrochemical reaction, assuming, diffuse double layer potential to be negligible, the rate equation can be

derived as

$$v_{\text{anod}} = k(A) \exp\left(\frac{-\Delta F^*}{RT}\right) \exp\left(\frac{\alpha n F \psi}{RT}\right) \quad \dots(1-5)$$

$$v_{\text{cath}} = k(C) \exp\left[\frac{-(\Delta F^* - \Delta F^0)}{RT}\right] \exp\left[\frac{-(1-\alpha)n F \psi}{RT}\right] \quad \dots(1-6)$$

where (A) and (C) are appropriate multiples of activity terms and

$$k = k_b T S / h \nu^* \quad \dots(1-7)$$

Let,

$$V = \psi - E_H \quad \dots(1-8)$$

and

$$\eta = V - E_r \quad \dots(1-9)$$

$E_H$  and  $E_r$  are the potentials of the standard hydrogen electrode and the reversible potential of the electrode in concern respectively.

For anodic current the rate expression in terms of current density

( $i = n' F v$ ,  $n'$  is the number of electrons transferred for one occurrence of the rate controlling step) will be (if  $n' = n$ )

$$\begin{aligned} i_a &= n F k(A) \exp\left(\frac{-\Delta F^*}{RT}\right) \exp\left[\frac{\alpha n F (V + E_H)}{RT}\right] \\ &= n F k(A) \exp\left(\frac{-\Delta F^*}{RT}\right) \exp\left[\frac{\alpha n F (\eta + E_r + E_H)}{RT}\right] \\ &= n F k(A) \exp\left[\frac{-(\Delta F^* - \alpha n F E_H - \alpha n F E_r)}{RT}\right] \exp\left(\frac{\alpha n F \eta}{RT}\right) \end{aligned} \quad \dots(1-10)$$

$E_r$  can be replaced from the formula

$$n F E_r = n F (E'_{ot} - E_H) - RT \ln \left[\frac{(A)}{(C)}\right] \quad \dots(1-11)$$

$E'_{ot}$  is the true standard state potential of the slow step.

$n F E'_{ot} = \Delta F'_0$  then,

$$\begin{aligned} i_a &= n F k(A) \exp\left[\frac{-(\Delta F^* - \alpha \Delta F'_0)}{RT}\right] \exp\left(\frac{\alpha n F \eta}{RT}\right) \left[\frac{(C)}{(A)}\right]^\alpha \\ &= n F k_1 (A)^{1-\alpha} (C)^\alpha \exp\left(\frac{-\alpha n F \eta}{RT}\right) \end{aligned} \quad \dots(1-12)$$



Similarly,

$$i_c = n F k_1 (A)^{1-\alpha} (C)^\alpha \exp \left( \frac{-(1-\alpha) n F \eta}{RT} \right) \quad \text{..(1-13)}$$

The net anodic current,  $i = i_a - i_c$ , and

$$i = n F k_1 (A)^{1-\alpha} (C)^\alpha \left[ \exp \left( \frac{\alpha n F \eta}{RT} \right) - \exp \left( \frac{-(1-\alpha) n F \eta}{RT} \right) \right] \quad \text{..(1-14)}$$

where

$$k_1 = \left( \frac{k_b T S}{h \gamma^*} \right) \exp \left( \frac{-(\Delta F^* - \alpha \Delta F'_o)}{RT} \right) \quad \text{..(1-15)}$$

At reversible potential the net anodic and cathodic currents are zero. The anodic current and cathodic current are then equal. This current, which flows with equal intensity anodically and cathodically, at  $E_r$  is specifically identified as the exchange current,  $i_o$ . The equation is then simplified as

$$i = i_o \left[ \exp \left( \frac{\alpha n F \eta}{RT} \right) - \exp \left( \frac{-(1-\alpha) n F \eta}{RT} \right) \right] \quad \text{..(1-16)}$$

where

$$i_o = n F k_1 (A)^{1-\alpha} (C)^\alpha \quad \text{..(1-17)}$$

The equation (1-16) is equivalent to the net anodic current. It may be simplified for situations in which the polarisation is small ( $\eta < 0.02$  V) or large ( $\eta > 0.05$  V). At low polarisation the exponential may be expanded and the current is given by the expression,

$$i = i_o \quad \eta n F / RT \quad \text{..(1-18)}$$

In the range of large polarisation the reverse reaction may be neglected and the equation (1-16) reduces to the Tafel equation

$$i = i_o \exp \left( \frac{\alpha n \eta F}{RT} \right) \quad \text{..(1-19)}$$

or

$$\eta = \frac{RT}{\alpha n F} \ln \frac{i}{i_0} \quad \dots(1-20a)$$

or

$$\eta = a + b \log i \quad \dots(1-20b)$$

where

$$a = \frac{RT}{\alpha n F} + 2.303 \left( \frac{RT}{\alpha n F} \right) \log i_0, \quad b = \frac{2.303 RT}{\alpha n F}$$

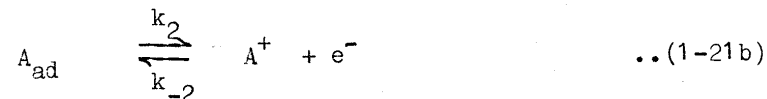
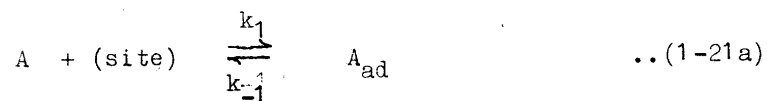
$$\text{If } \alpha = 1/2, \quad n = 1, \quad T = 298^\circ\text{K}$$

$$b = 0.118 \text{ V} / \text{current decade.}$$

#### The role of chemisorption :

In a fuel cell electrode process the reactant is assumed to be adsorbed at an active site on the electrode prior to electron transfer or surface reaction. Activation energy of adsorption of the reactant on the electrode may be of considerable value, presenting a formidable barrier to high currents. Further limitations occur if the surface is covered with products that are difficult to desorb or poisons that reduce the number of active sites. So, it is possible that the rate of chemisorption may be the slowest reaction step and, therefore, the sole source of polarisation. Chemisorption polarisation has been discussed in details by Austin<sup>10</sup>. In the following treatment Langmuir's theory of adsorption has been postulated.

The electrochemical reaction may be assumed to follow through the steps : first, adsorption on a surface site to form the surface complex, and second, ionisation.



At open circuit, both steps equilibrate after sufficient time so that an overall equilibrium between the molecular reactant and the ions, and electrons is established. When current is drawn the equilibrium is upset. If chemisorption is slow in comparison to ionisation, the adsorbate concentration will decrease and the potential will change as the electrochemical step adjusts its rate to maintain the current.

Let  $p$  be the partial pressure of A and  $\theta$  be the fraction of sites covered by A at a given current,  $i$ , then

$$\frac{d\theta}{dt} = k_1 p(1-\theta) - k_{-1} \theta - k_2 \theta = 0 \quad \dots(1-22)$$

or

$$\theta = (k_1 p) / (k_{-1} + k_2 + k_1 p) \quad \dots(1-23)$$

$$\text{current, } i = F k_2 \theta = F k_2 k_1 p / (k_{-1} + k_2 + k_1 p) \quad \dots(1-24)$$

However, the rate constant for ionisation of A is dependent on the electrode potential

$$k_2 = k \exp \left[ \frac{\alpha F \psi'}{RT} \right] \quad \dots(1-25)$$

where  $\psi'$  is the potential difference between the solution and the electrode surface. Then

$$i = \frac{F k_1 k \exp \left[ \frac{\alpha F \psi'}{RT} \right] p}{k_{-1} + k \exp \left[ \frac{\alpha F \psi'}{RT} \right] + k_1 p} \quad \dots(1-26)$$

The current from an electrode which is chemisorption polarised is

thus a function of reactant pressure and polarisation.

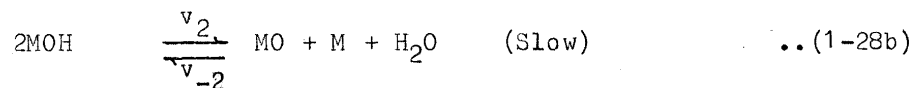
The equation (1-26) can be transformed to

$$\eta = \frac{RT}{\alpha F} \ln \frac{1}{k} - E_0 + \frac{RT}{\alpha F} \ln \frac{(k_{-1} + k_1 p) i}{(F k_1 p - i)} \quad \dots (1-27)$$

where  $\eta = \psi' - E_0$ . The equation (1-27) gives the measure of polarisation of a chemisorption - limited electrode. ( $\psi' = \psi$ ).

#### Surface reaction :

The reaction between discharged ions, particularly if there is a strong bonding between the surface and the radicals, may be considerably slower than the preceding steps. For example, in hydrogen evolution on platinum, the classical interpretation proposed by Tafel and modified by other investigators<sup>11</sup> postulates that the rate - limiting reaction is the surface combination of discharged ions. Bockris<sup>12</sup> treated surface reaction controlled electrode processes. He derived rate equations for oxygen evolution assuming various mechanisms. One model suggested is



With usual notations, the rate equation for hydroxyl discharge is

$$v_1 = k_1 (1 - \theta_{\text{MOH}}) a_{\text{OH}^-} \exp \left[ \frac{F\psi'}{2RT} \right] \quad \dots (1-29)$$

where  $\alpha = 1/2$  for an electron transfer reaction. The rate

equations for ionisation and hydroxide decomposition are given by

$$v_{-1} = k_{-1} a_{\text{MOH}} \exp \left[ \frac{-F\psi'}{2RT} \right] \quad \dots(1-30)$$

$$v_2 = k_2 a_{\text{MOH}}^2 \quad \dots(1-31)$$

$$v_{-2} = k_{-2} a_{\text{MO}} \quad \dots(1-32)$$

for constant water and metal activity. The oxygen evolution and dissolution rates are

$$v_3 = k_3 a_{\text{MO}}^2 \quad \dots(1-33)$$

$$v_{-3} = k_{-3} \quad \dots(1-34)$$

since the oxygen pressure is constant. The equation derived for the rate of oxygen evolution in terms of current is

$$i = 2F (K_1)^2 a_{\text{OH}^-}^2 \exp \left[ \frac{2F\psi'}{RT} \right] \quad \dots(1-35)$$

or the polarisation equation is (where  $K_1 = k_1/k_{-1}$ )

$$\eta = \frac{RT}{2F} \ln \frac{1}{2F K_1 a_{\text{OH}^-}^2} - E_0 + \frac{RT}{2F} \ln i \quad \dots(1-36)$$

or  $\eta = a + b \log i \quad \dots(1-20b)$

Tafel slope (b) for such reaction is 0.03 at 25°C for low polarisation.

### C. The Catalysts for Hydrogen and Other Fuel Electrodes :

At normal temperatures, chemisorption of hydrogen of the type required for high catalytic activity is dissociative, and involves the formation of a partially covalent surface bond between

hydrogen atom and the d electron of the metal. The extent to which the d electron orbitals of a metal are filled may be defined as d-band character of the metal. The percentage d-band character of a metal can be related to the adsorption energy and the work function of the metal. Metals having a lower percentage of d-band character, (or more holes in the d-band), have more unpaired electrons. These vacant orbitals are capable of reacting with electron donors ( say  $H_2$  ) and thus adsorbing the donor strongly. Therefore, the lower the percentage of d-band character, the greater are the adsorption tendency and heat of chemisorption. In this respect iron, cobalt, nickel which adsorb hydrogen strongly appear to be not good catalyst. On the otherhand metals of platinum group having greater d-band character found to be effective catalyst.

The electronic work function increases with d-band character. This is because electron species are paired as the d-band vacancies are filled. These electrons are more stable and require greater energies for their extraction from the metal. Thus, the heat of adsorption (chemisorption) decreases as the work function increases. Conway and Bockris<sup>13</sup> observed a correlation between reaction rate and the work function of the metal for the hydrogen evolution reaction. Exchange current increases exponentially with the work function for certain metals ( electrochemical mechanism) but otherwise with metals when the reaction rate is controlled by slow electron transfer.

In addition to the electronic factors, geometric factors should also be influential in the catalysis of electrode reactions.

By geometric factors we mean the interatomic spacing and arrangement with catalyst lattice. The spacing of atoms must be expected to affect the activation energy of reaction. Sherman and Eyring<sup>14</sup> have made quantum mechanical calculations for adsorption of hydrogen on graphite. It was found that the activation energy of adsorption of hydrogen was a minimum for a certain atomic spacing (3-5 Å). At larger distance the energy is higher because the molecule must be dissociated prior to adsorption; at smaller spacings repulsion forces retard adsorption.

In recent years, the anodic oxidation of methanol, formic acid, hydrazine and formaldehyde on platinum, in both acidic and basic media, has been studied in considerable detail. The impetus for these investigation is derived from a search for suitable fuels to replace hydrogen in the fuel cell. Breiter et al<sup>15</sup> studied the oxidation processes in acid solution. These authors propose that the initial step in the reaction is the direct oxidation of methanol to methoxyl radical and a hydrogen ion.

The anodic oxidation of methanol in alkaline solution has been studied by Vielstich<sup>16</sup>, and Buck and Griffith<sup>17</sup>. Vielstich<sup>16</sup> concludes that platinum reacts to form platinum hydroxide which in turn oxidises the methanol chemically. Buck and Griffith<sup>17</sup> conclude that the rate determining step in alkaline solution involves the reaction of a methoxide and two hydroxide ions with the transfer of two electrons. Liang and Franklin<sup>18</sup> studied the anodic oxidation of formic acid and formaldehyde in addition to methanol. Other investigators are Oxley<sup>19</sup> and Giner<sup>20</sup>. Grimes and Spengler<sup>21</sup> observed that in formate ion oxidation, platinum and palladium are the best anode catalyst. At 30°C, palladium was

the best anode catalyst and the activity decreased with an increase of platinum content in Pt-Pd system. Various catalysts have been used in electrodes of alkaline liquid fuel cells<sup>22</sup>. Yamano and Ikeda<sup>23</sup> have used typical alkaline - resistant metals i.e., Au, Ag, Pt, Pd, Ni and Cu as catalyst metals. They have used formaldehyde, hydrazine and methanol as liquid fuels which are conventional and typical fuels. Their results showed that Pt, Pd and Au powders are preferable catalysts. In formaldehyde oxidation they found the order of preference is Au, Pt, Pd, Ag, Ni and Cu for the metal catalysts. That for hydrazine, the order is Ni, Pt, Pd, Cu, Au and Ag. With regard to methanol Pt, Pd and Au are good catalysts. Binder and co-workers<sup>24</sup> showed that the order of the activity of platinum metals in the oxidation of methanol in the KOH solution is  $Pt > Pd > Ru = Rh > Ir > Os > Au$ . The values differ from that of Tanaka<sup>25</sup>. Former authors prepared the catalyst by Raney method ( containing aluminium 0.1 to 1 % ). In acid solution the order of the activity is  $Os > Ru = Ir > Pt > Rh > Pd$  differing from Breiter's values<sup>26</sup>. They tried to explain the activity in terms of paramagnetic susceptibility. Palladium with largest susceptibility (quasi-ferromagnetic region) value is the least active catalyst. They found that Ru - Pt alloys are almost specific for the conversion of methanol. These catalysts have also been found to be superior to platinum in other reactions<sup>27</sup>. These results may be due to optimum value of susceptibility leading to optimum sorption of all reactants. Further references on the excellent properties of Pt - Ru catalyst in anodic oxidation of methanol have been mentioned by Heath<sup>28</sup>, Takamura and Minamiyama<sup>29</sup> observed that complete oxidation of methanol to carbonate ion takes



place on palladium in alkaline medium. Several studies have been reported on the mechanism of the anodic oxidation of methanol at platinum electrode both in acidic and alkaline media<sup>30</sup>.

Dahms and Bockris<sup>31</sup> studied the relative electrocatalytic activity of noble metals in the oxidation of ethylene in acid medium. They observed complete oxidation of ethylene to  $\text{CO}_2$  on Pt, Ir and Rh. On Au and Pd main products are aldehydes and acetones. The order of activity is  $\text{Pt} > \text{Rh} > \text{Ir}$  and  $\text{Pd} > \text{Au}$  in this group of metals.

In the study of mixed catalysts, Frumkin<sup>32</sup> observed that an alloy made by simultaneous deposition of platinum and ruthenium from a mixture which contained about 10 per cent or less ruthenium was 100 times as active as pure platinum in oxidation of methanol. McKee and Pak<sup>33</sup> found that certain metals such as Ni, Cu, Sb, in low percentage ( 5 - 10 % ) mixed with platinum are better catalyst than platinum alone in oxidation of  $\text{H}_2$  and CO mixture containing upto 10 per cent CO.

Shropsire<sup>34</sup> observed that molybdate and perrhenate in solution improved the catalytic properties of platinum for the oxidation of methanol and formaldehyde in sulphuric acid medium. Decreased polarisation has been shown to result from a cycle involving chemical reaction of the fuels with an oxidised molybdate species with subsequent electro-oxidation of the reduced molybdate. The process requires the adsorption of molybdate at the electrode surface through out the anodic cycle. Similar mechanism was suggested for Re (VIII).

For hydrazine anode, Gillibrand and Lomax<sup>3</sup> used porous nickel plates containing catalyst. Jasinski<sup>35</sup> used Pt, Pd and nickel boride as catalysts for hydrazine anode in alkaline medium. It appears that nickel boride is a superior catalyst.

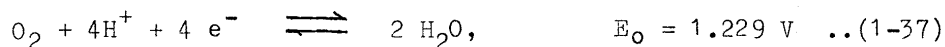
For formic acid or formate ion anode, Binder and co-workers<sup>36</sup> used porous disks with a heavy loading of Raney platinum. Jasinski and co-workers<sup>4</sup> used porous platinum black flow by electrodes, 7.5 x 7.5 cm in active area, were bonded with PTFE to a tantalum screen and pressed against the matrix ( probably asbestos ) that contained the electrolyte, 30 W/O H<sub>2</sub>SO<sub>4</sub>. Grimes and Spengler<sup>21</sup> used nickel plaques containing platinum black.

#### D. The Cathodic Reduction of Oxygen :

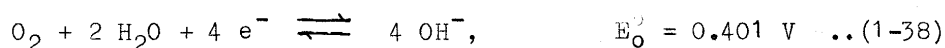
In recent years, much interest in fuel cells has promoted a vigorous investigation of the electrochemical reduction of oxygen and oxidation of hydrogen or liquid fuel on noble metals. Noble metals are constituents of the fuel cathode and anode. Electroanalytical chemists are also interested in these processes, as noble metal electrodes are used as indicator electrodes. It is necessary to have some understanding of the nature of the electrode surface, the type of adsorbed film and the extent of surface coverage for the elucidation of the mechanism of any electrochemical process that takes place on these electrodes.

Considerable amount of work has been done on the oxidation and reduction of oxygen on a platinum electrode. Some investigators<sup>37</sup> have detected the presence of H<sub>2</sub>O<sub>2</sub> intermediates in this system . while others<sup>38</sup> have not. The overall electrochemical reaction

for this oxygen electrode is



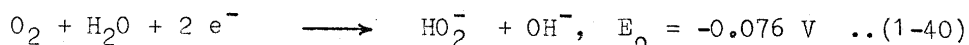
in acid solution,



in alkaline solution. For hydrogen electrode in alkaline solution the reaction is



However, in aqueous electrolyte fuel cells operating anywhere between room temperature, the oxygen electrode mechanism is somewhat complex and the potential values as given in above equations are not achievable. The classical work of Berl<sup>39</sup> has shown that true primary oxygen electrode mechanism involves a peroxide ion product according to the equation



In practice peroxide decomposing catalyst at the electrode modifies the potential towards the theoretical value. When carbon electrode is used for oxygen cathodes, peroxide decomposing catalysts are often incorporated, so that the  $\text{HO}_2^-$  activity is depressed to the extremely low value. The potential associated with the equation ( $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{HO}_2^- + \text{OH}^-$ ) would then be same as that predicted for overall four electron processes. Practically the potential is nearly at least 0.1 V more cathodic than reversible value for four electron reduction. The effect of hydrogen peroxide concentration in the electrolyte has been studied by Yeager and co-workers<sup>40</sup> and Vielstich<sup>41</sup>. Hunger and Marko<sup>42</sup> showed that a minimum half-life of peroxide is observed

at pH 14 and change of the half-life to different magnitudes with different catalyst. At pH value less than 13, a catalyst is not effective to prevent the increase of half-life of  $H_2O_2$  to values one hundred to one thousand fold than that at pH 14. It is believed that this is the reason why oxygen electrodes do not operate well in neutral or acidic electrolytes.

The value observed for oxygen electrode potential on noble metal electrodes (Ag, Au, Pt), and with increasing temperature, is between peroxide potential and the four electron oxygen potential. In the temperature region 200 to 500°C, it can be assumed that the reaction will almost entirely follow the four electron process.

In practical fuel cells, oxygen electrode is prepared by depositing catalyst on a very good conductive porous carbon electrode. The process consists of soaking carbon electrode body in a solution of heat decomposable, oxidising heavy metal salt, and subsequent heating of the cathode<sup>43</sup>.

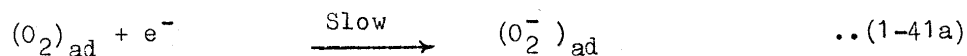
#### Reduction of oxygen at platinum electrode :

Hoare and others<sup>37b, 44</sup> observed that when a complete layer of electronically adsorbed oxygen is formed on a platinum surface, produced by anodisation, heating in  $O_2$  or by treating in  $HNO_3$ , the reversible  $O_2$  potential is obtained. Otherwise at noble metal electrodes, the rest potential is a mixed potential. In the former case, the electrode is designated by the symbol  $Pt(O)/O_2$ . A higher potential near 1.6 V on oxygen electrode has been obtained by Criddle<sup>45</sup>. The surface state of platinum in that case is described as  $PtO_x$ , where  $x$  equals or exceeds 2. All

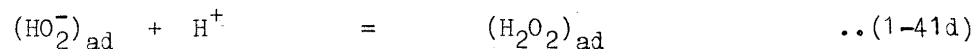
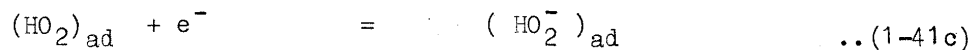
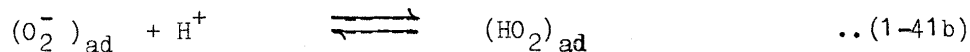
these works indicate that adsorbed oxygen or surface oxide<sup>46</sup> formed on platinum has the ability to transfer charge from the metal to a reactant in the solution without an appreciable increase in the thickness of the film. The presence of the surface oxide alters the behaviour of platinum indicator electrodes in potentiometry<sup>47</sup>, chronopotentiometry<sup>46a</sup>, polarography<sup>48</sup> and kinetics determination<sup>37a</sup>.

A knowledge of the chemical nature of the surface oxide as well as the mechanism of its formation and reduction is a prerequisite to the understanding of the behaviour of platinum electrode as a cathode in fuel cell or an indicator electrode.

The cathodic polarisation curves on Pt in acid solution<sup>49</sup> exhibit Tafel regions with a slope of about 0.1 V. So it may be assumed that a one electron transfer reaction involving the molecular oxygen is the rate determining step for the reduction of O<sub>2</sub> on Pt in acid solution at current densities greater than 10<sup>-6</sup> A/cm<sup>2</sup>. According to Hoare most likely the step is

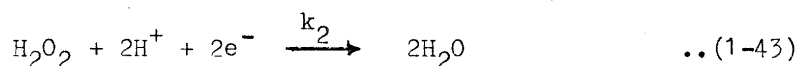
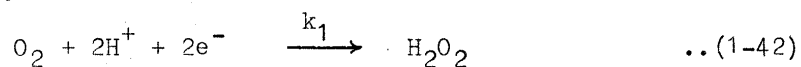


succeeding steps are



Yeager and co-workers<sup>50</sup> observed a steady state concentration of H<sub>2</sub>O<sub>2</sub> at Pt cathodes in KOH. Platinum is known to be good

peroxide decomposing catalyst and so  $\text{H}_2\text{O}_2$  is decomposed by an electrochemical local cell mechanism<sup>51</sup> or chemically on adsorbed oxygen film (Pt-O) as suggested by Bianchi<sup>52</sup>. In any event when  $\text{H}_2\text{O}_2$  is decomposed to oxygen, which repeats the reaction scheme and effectively four electrons are transferred and  $\text{H}_2\text{O}$  is the end product of  $\text{O}_2$  reduction. Using a platinum rotating ring electrode, Myüller and Nekrasov<sup>53</sup> found that the reduction of  $\text{O}_2$  takes place in two stages



As an important point in this work, the specific rate for reduction of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$ ,  $k_2$ , is an order of magnitude larger than the specific rate for reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$ ,  $k_1$ , on oxidised Pt; but  $k_1 > k_2$  on reduced platinum.

It is also to be noted that the presence of adsorbed oxygen on Pt-surface inhibits the reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$ <sup>54</sup>, but promotes the catalytic decomposition of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$ <sup>52,53</sup>.

The reduction of  $\text{O}_2$  was carried out on Pt-O-alloy<sup>44b</sup> which was made by  $\text{HNO}_3$  treatment, and results show that Pt-O-alloy surface is a better catalyst for the reduction of  $\text{O}_2$  (appears from polarisation study), probably the adsorbed  $\text{O}_2$  facilitates the transfer of electron. In addition, it was found that the Pt-O-alloy surface is a better catalyst for the decomposition of  $\text{H}_2\text{O}_2$ .

With extended cathodic polarisation, the magnitude of the steady state concentration of  $\text{H}_2\text{O}_2$  detected in the electrolyte is

a function of the catalytic activity of the electrode surface for the decomposition of  $\text{H}_2\text{O}_2$ <sup>55</sup>. This concentration is high for carbon electrode, less for  $\text{Au}$ <sup>56</sup>, small for  $\text{Pt}$ <sup>49</sup> and below detection for  $\text{Pt-O-alloy}$ <sup>44b</sup>.

Bagotskii, et al<sup>57</sup> and Sandler, et al<sup>58</sup> found that the electrode pretreatment greatly affects the kinetics of the reduction of  $\text{O}_2$  on Pt cathodes.

Much work has also been done with other noble metals such as  $\text{Pd}$ <sup>59</sup> and  $\text{Au}$ <sup>60</sup> which could be used as inert materials for fuel cathode or indicator electrodes.

Reduction of  $\text{O}_2$  at palladium electrode :

The experimental observations of the dependence of  $\eta$  on partial pressure of oxygen, and the finding of a Tafel slope of 0.12 support the view that the mechanism of  $\text{O}_2$  reduction on Pd cathodes in acid solution is the same as that on Pt cathode.<sup>61</sup> The first step of reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  is hindered by the presence of  $\text{O}_2$  on the Pd surface, but the second step of  $\text{H}_2\text{O}_2$  to water, is promoted by the adsorbed layer of  $\text{O}_2$ <sup>62</sup>. An explanation which is the same as the one accounting for similar results on preanodised Pt cathodes, may be used for Pd cathodes.

In alkaline solution, the  $\eta$  is lower than the acid solution. Sobol and co-workers<sup>62</sup> suggest that the interference of adsorbed anions with oxygen reduction processes at Pd cathodes in acid solution causes the  $\eta$  to be higher than in alkaline solution.

### Reduction of O<sub>2</sub> at gold electrodes :

Investigation of the reduction of O<sub>2</sub> at gold electrodes in acid and alkaline solutions<sup>56,63</sup> show that  $\eta$  is higher on Au than on Pt cathode and that peroxide was detected as a stable intermediate. Rao and co-workers<sup>64</sup> observed that the coverage of the Au surface with adsorbed oxygen is probably no greater than about 3 per cent, which is not enough to produce a measurable influence on the polarisation curve in reduction of O<sub>2</sub>. These experimental observations indicate that the reduction of O<sub>2</sub> takes place through the formation of intermediate H<sub>2</sub>O<sub>2</sub>. As gold is poorer catalyst than platinum in decomposition of H<sub>2</sub>O<sub>2</sub>, the steady state concentration of H<sub>2</sub>O<sub>2</sub> is about 10<sup>-4</sup> M. In alkaline solutions the reduction of O<sub>2</sub> takes place at lower  $\eta$  values.

### E. Noble Metal Electrodes Used as Anode :

The results of the early work clearly showed that the noble metals interact with O<sub>2</sub>, and thin films are formed on the surface. In the understanding of the nature of O<sub>2</sub> electrode, it is essential to determine the nature of thin films ~~adsorbed~~ on the noble metal surface.

#### Platinum electrode :

The presence of adsorbed oxygen films on Pt electrodes has been proved from the constant current charging curve technique<sup>65</sup> in which the electrode system is anodised or cathodised at a constant current in acid. The potential-time (coulombic charge) curve gives information for the potential determining species adsorbed on the electrode surface. A general nature of the curves

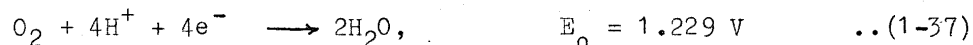


has been shown in Fig. 1-1-2. Initial stage of the anodic branch is the hydrogen ionisation region (about 0.4 V vs. N.H.E., the limit of hydrogen adsorption). The potential then rises abruptly from about 0.4 V to about 0.8 V, where oxygen is first adsorbed. This region is due to the charging of the double layer. Starting at a potential of about 0.8 V, a linear increase in potential with time is observed which may be called the oxygen adsorption region. The curve becomes nearly flat above 1.6 V where the evolution of oxygen gas begins ( plateaus appearing in this region indicate the different species, if any, adsorbed on the electrode surface ). After the potential is reached where oxygen is evolved, the current is reversed and a constant cathodic current is applied to the electrode. The potential - time curve is then recorded. The region for flat plateau with curve somewhat below 0.8 V is the one where oxygen/oxide layer is stripped from the electrode surface. The potential then falls to a value where hydrogen gas is evolved.

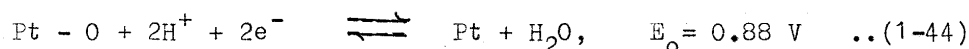
Butler and co-workers<sup>46b,66</sup> observed that one atom of adsorbed oxygen is associated with one surface atom of Pt. Since the amount of adsorbed oxygen atom may be determined from the charging curve, a measure of true surface area may be made. Schuldiner and Roe<sup>67</sup> applied this principle in determining true electrode area from the oscilloscopic trace of charging curve. Many investigators<sup>46b,c,e,68</sup> have found one adsorption region in the anodic and one reduction plateau in the cathodic charging curve. However, Wakkad and Emara<sup>69</sup> observed more than one arrest in the anodic branch but only one reduction step in the cathodic branch using low current densities (  $\sim 1 \mu\text{A}/\text{cm}^2$  ). Lee and co-workers<sup>70</sup> also found the arrests in the potential-time curve of

Pt electrode in the process of chemical reduction of the preoxidised (chemically) platinum electrode. These arrests according to them correspond to Pt at different oxidation states. In both cases above, the first arrest is correlated with the appearance of a film of PtO at about 0.82 V and the second with a film of PtO<sub>2</sub> at about 1.05 V. Above views are controversial. It is still more contradictory as the value of  $Q_a/Q_c \approx Q_a$  coulombic charge for the formation of oxygen layer in the process of charging,  $Q_c$  is charge to remove that layer during the cathodic process <sup>7</sup> in most investigations <sup>46b,68,71</sup> is found to be equal to 2, but the value approaches to 1 with higher current density and repeated cycles of polarisation.

The observed steady state rest potential of a Pt electrode to be 1.06 V instead of 1.229 V, the theoretical value is explained by mixed potential theory <sup>46f</sup>. The potential was concluded to be a mixed potential involving O<sub>2</sub>/H<sub>2</sub>O reduction;



and a Pt/Pt-O reaction;



where Pt-O represents a layer of adsorbed oxygen atoms on the Pt-surface. A local cell is being operative, depressing the O<sub>2</sub>/H<sub>2</sub>O theoretical potential value. Another explanation is given by oxide theory. Other investigators <sup>46e,h,72</sup> think that at potentials below about one volt the adsorbed oxygen is in the form of PtO and above this value, in the form of a mixture of PtO and PtO<sub>2</sub>. Mayell and Langer <sup>72c</sup> reported that oxygen may be adsorbed at Pt in a variety of forms, Pt(OH)<sub>2</sub>, Pt(O)<sub>2</sub>, PtO, tight PtO, Pt(O)<sub>2.5</sub> and Pt(O)<sub>4</sub>. Potentials 1.24 V and 1.54 V were associated

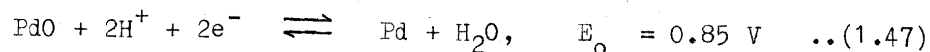
with  $\text{Pt}(\text{OH})_2$  and  $\text{Pt}(\text{O}_2)$  ( as there is evidence<sup>46e,73</sup> that oxygen may be dissolved in Pt, the different oxides of Pt may be interpreted in terms of different extent of oxygen adsorption).

Foregoing discussions indicate that reversible oxygen potential can be obtained when the platinum surface is covered with a complete layer of Pt-O, which is an electronically conducting film formed by preanodisation or by nitric acid treatment<sup>44a,c</sup>.

Data obtained from charging curves and potential sweep traces indicate that the nature of the Pt-O<sub>2</sub> system is essentially same in acid and alkaline medium.

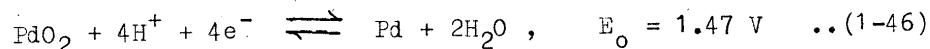
#### Palladium electrode :

There is evidence<sup>46c,59a,b,74,75</sup> from charging curves that two oxides, PdO and PdO<sub>2</sub>, may be formed on Pd electrodes. On Pd electrodes in acid solution, Vetter and Berndt<sup>46c</sup> found that  $Q_a = 2 Q_c$ , at slow charging rates. But Hickling and Vrjosek<sup>59b</sup> observed  $Q_c = Q_a$  at high charging rates. When an oxide - free Pd is placed in O<sub>2</sub> - saturated peroxide free acid solution, a steady state rest potential of about 0.87 V is observed<sup>59c</sup>. Hickling and Vrjosek<sup>59b</sup> reported the standard potential of Pd/PdO electrode reaction

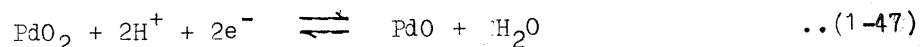


Initially the rest potential depends on pH, but as PdO layer builds up the potential becomes independent of pH. For the

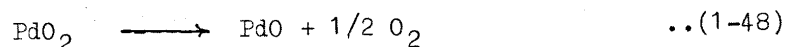
Pd/PdO<sub>2</sub> electrode reaction<sup>59c</sup> is



Butler and Drever<sup>75</sup> concluded that during charging process the layer of PdO initially formed was converted to PdO<sub>2</sub> when evolution of O<sub>2</sub> was reached, but PdO<sub>2</sub> decomposed spontaneously on open circuit. With time the potential falls from 1.47 V value to a steady one 0.87 V<sup>59c</sup> through the following reaction<sup>59a</sup>,



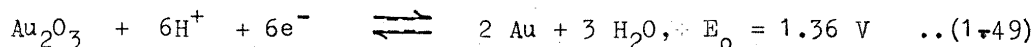
Hoare<sup>59c</sup> proposed that PdO<sub>2</sub> is unstable and decomposes to PdO accompanied by the evolution of O<sub>2</sub>



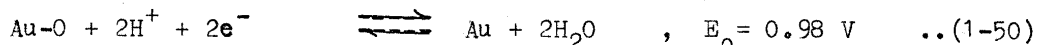
#### Gold electrode :

The rest potential of an oxide - free Au electrode in oxygen saturated acid solution is between 0.7 to 0.8 V vs. hydrogen electrode which drifts<sup>60c</sup> to a steady value of about 0.98 V<sup>60c</sup>. This potential is for the Au/AuO system. When Au surface is anodically polarised, potential about 1.36 V for the Au/Au<sub>2</sub>O<sub>3</sub> system is reported<sup>60a,c,76,77</sup> (Au<sub>2</sub>O<sub>3</sub> begins to form). When a gold wire electrode is used to make contact with a slurry of Au<sub>2</sub>O<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> solution, a potential of about 1.36 V is obtained.<sup>78</sup> Wakkad and El Din<sup>60b</sup> in their anodic charging curve at low current density reported the presence of Au<sub>2</sub>O, AuO and Au<sub>2</sub>O<sub>3</sub> in acid solution corresponding to 0.36 V, 0.98 V and 1.30 V. The cathodic charging curve showed the reduction of Au<sub>2</sub>O<sub>3</sub> step and

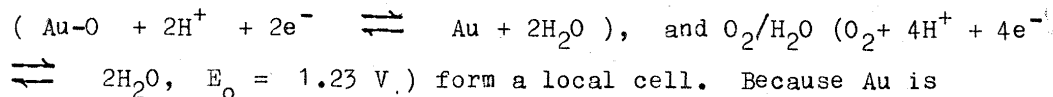
that the potential fell to a value more positive than that of Au-Au<sub>2</sub>O system ( showing no step for Au-AuO system). Vetter and Berndt<sup>46c</sup> observed first Au-O layer formed by anodic polarization converted to a Au<sub>2</sub>O<sub>3</sub> which continued to grow with further polarisation. They also observed that  $Q_a > Q_c$ . But at low<sup>71</sup> current density  $Q_a \approx Q_c$ . At higher charging rate, the step corresponding to Au/Au<sub>λ</sub>O is absent. The reaction of the Au/Au<sub>2</sub>O<sub>3</sub> system is



and that for Au/Au<sub>λ</sub>O system is



Both potentials of Au/Au<sub>2</sub>O<sub>3</sub> and Au/Au-O are independent of partial pressure of O<sub>2</sub>, and the potentials vary by 60 mV per unit of pH<sup>60c</sup>. Hoare<sup>60c</sup> explains 0.98 V by the concept of mixed potential. It has been assumed that Au/Au-O



form a local cell. Because Au is a poor catalyst for O<sub>2</sub>/H<sub>2</sub>O reaction in H<sub>2</sub>O<sub>2</sub> decomposition, it is strongly polarised; a mixed potential sets in showing an intermediate value of 0.98 V. Variation of the rest potential with time may be traced to changes in the activity of the Au-O layer with the amount of oxygen adsorbed on Au-surface. The reversible oxygen potential is not observed on Au.

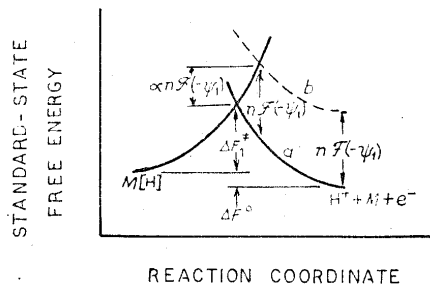


Fig. 1-1-1 Effect of voltage on standard-state free energies of  $H^+$  and chemisorbed H.

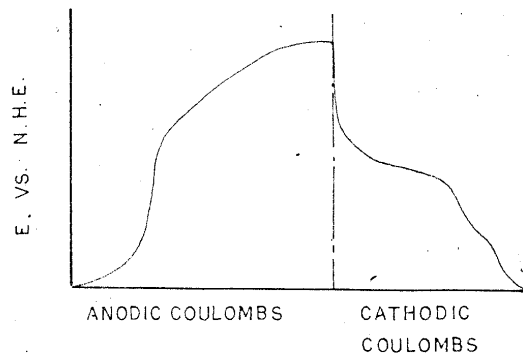


Fig. 1-1-2 Anodic and cathodic charging curves