

Electrocatalysis

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A. Basic Concepts:

Electrocatalysis is enhancement of electrode kinetics by a material by minimizing the overpotential.

Overpotential is the extra potential over the equilibrium value that must be applied to cause an electrodic reaction at a certain rate. An electrodic reaction may be anodic (oxidation) or cathodic (reduction) depending upon the direction of overpotential with respect to the equilibrium potential of the electrode.

i. Equilibrium at an Electrode

The equilibrium at an electrode may be illustrated with respect to a metal dipped in a solution of its ions e.g. $Zn(s)/Zn^{2+}(aq)$ or $Ag(s)/Ag^{1+}(aq)$ or $Pt/Fe^{2+}, Fe^{3+}(aq)$ or $Pt, H_2(g)/H^+(aq)$ etc. Let Fig.1 represent equilibrium of the type $M(s) \leftrightarrow M^{n+} + n e^-$ (e.g. $Zn(s) \leftrightarrow Zn^{2+} + 2e^-$).

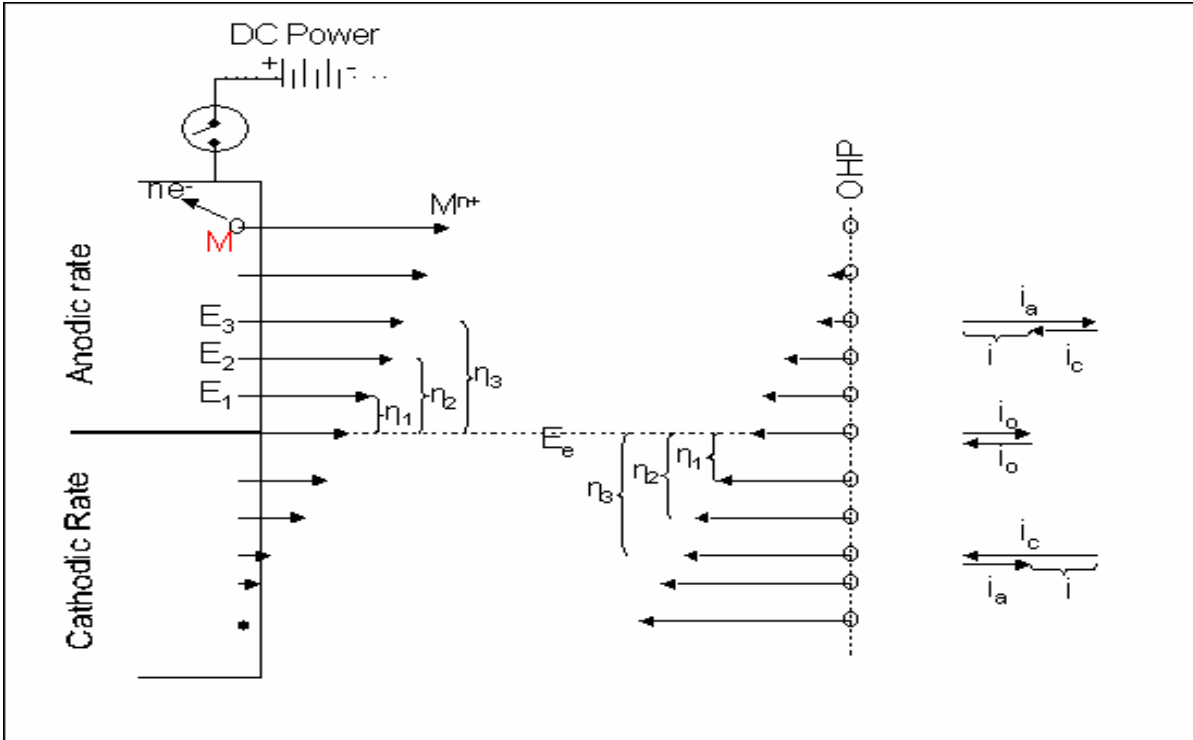


Fig.1. Illustration of equilibrium at an electrode

In the beginning $Zn(s)$ will undergo oxidation at a rapid rate sending additional Zn^{2+} ions in solution and electrons on the metallic electrode. The rate of oxidation (anodic process) will diminish as excess positive charge accumulates in the solution. This is signified by the decreasing magnitude of (\rightarrow) in Fig.1. Conversely as electrons get accumulated on the metal, the ions from the solution get reattracted (\leftarrow) and align in the OHP resulting in the formation of electrical double layer (an electrified interface). If there is contact adsorption of ions, the electrified interface behaves as a triple layer.

At a certain stage the two rates become equal and equilibrium is established at the electrode. The potential acquired by the electrode at equilibrium is known as equilibrium potential E_e . Overpotential is then the departure of electrode potential from its equilibrium value and given by $\eta = (E - E_e)$. Both the anodic and cathodic currents are equal ($i_a = i_c$) at equilibrium and is known as exchange current density i_0 for an electrode of unit area. Net anodic or cathodic currents can be obtained by applying suitable overpotentials. This may be achieved by connecting the electrode to the positive or the

negative of the dc power supply (Fig. 1). Fig.2. illustrates the structure of electrified interface

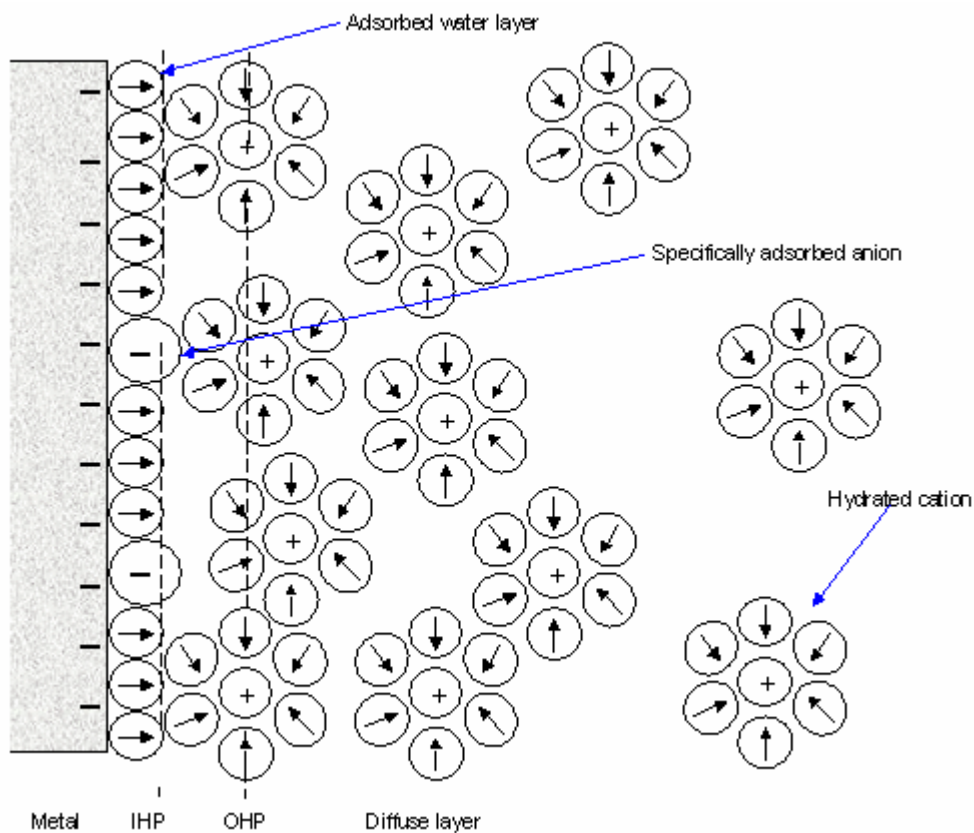


Fig. 2 Illustrates the BDM model of the interface.

ii. Electron Transfer

Fig.3 illustrates the charge transfer energetics at a metal electrode. As the charge on the metal becomes more negative, the Fermi level (E_F) gets raised and electrons transfer from Fermi level to the LUMO (Lowest Unoccupied Molecular Orbital). In such a case the species from the solution undergoes reduction. The rate of reduction will increase as the gap between E_F and LUMO widens. When $E_F < \text{HOMO}$ (Highest Occupied Molecular Orbital), the solute species undergoes oxidation by transferring electrons to Fermi level. E_F gets raised and hence the potential of the electrode changes (becomes less positive). If however the potential of the working electrode is controlled, the electrons given to the electrode are drained off as current through the cell. The opposite process would occur at the counter electrode.

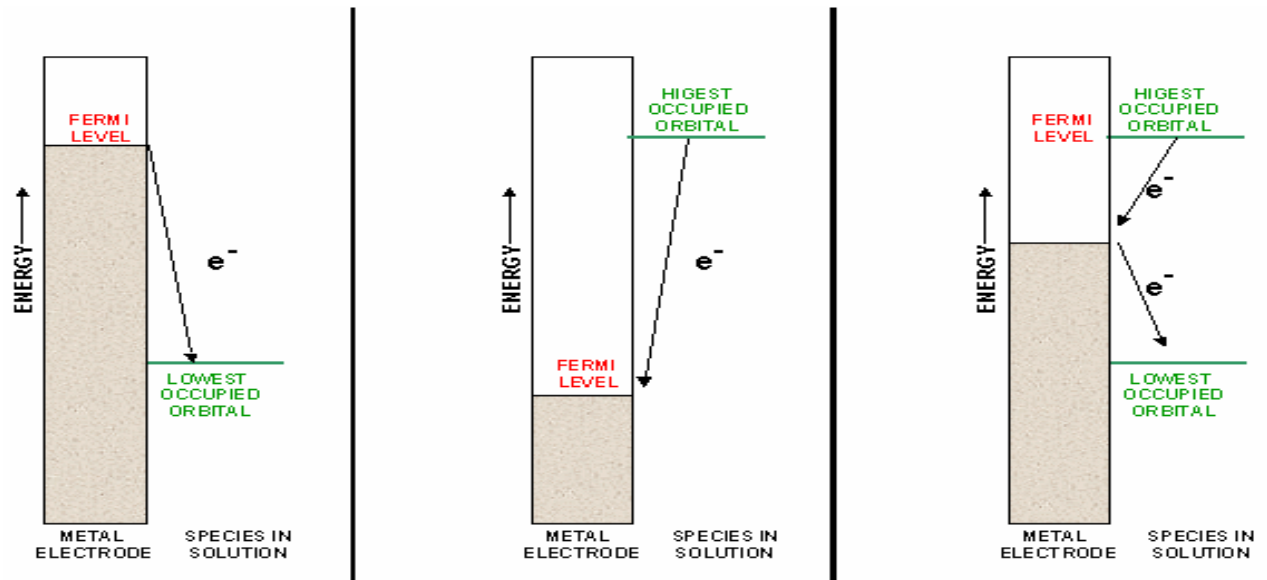


Fig. 3 Charge transfer energetics at a metal electrode

Current – Potential Relationships

There exists a simple mathematical relationship between current and overpotential and is known as Butler – Volmer equation. It is given by

$$i = i_0 [e^{(1-\alpha)\eta f} - e^{-\alpha\eta f}] \dots\dots\dots(1)$$

where α is known as transfer coefficient, η is overpotential and $f = F/RT$. For one electron transfer reaction often symbol β is used in place of α . β is known as symmetry factor. Both β or α combine with overpotential to determine the magnitude of electrical energy supplied to the electrode to obtain the desired current. The terms in eqn.1 are illustrated graphically in Fig.4.

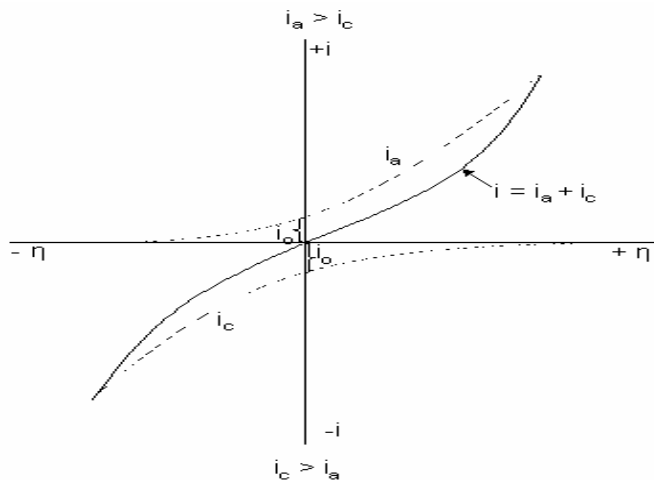


Fig.4. Graphical representation of the Butler - Volmer equation

At low overpotentials ($\eta < 10\text{mV}$), eqn.1 simplifies to $R_{ct} = 1/i_0f$ (2), where R_{ct} is charge transfer resistance at the electrode. Similarly at high overpotentials ($\eta > 50\text{mV}$), eqn.1 can be rearranged in the form $\eta = a + b \log i$ (3) and is known as Tafel law. It is valid both for anodic and cathodic processes. Currents at various overpotentials can be measured at a working electrode which contains the electro-catalytic material in a three electrode assembly of the type shown in Fig.5.

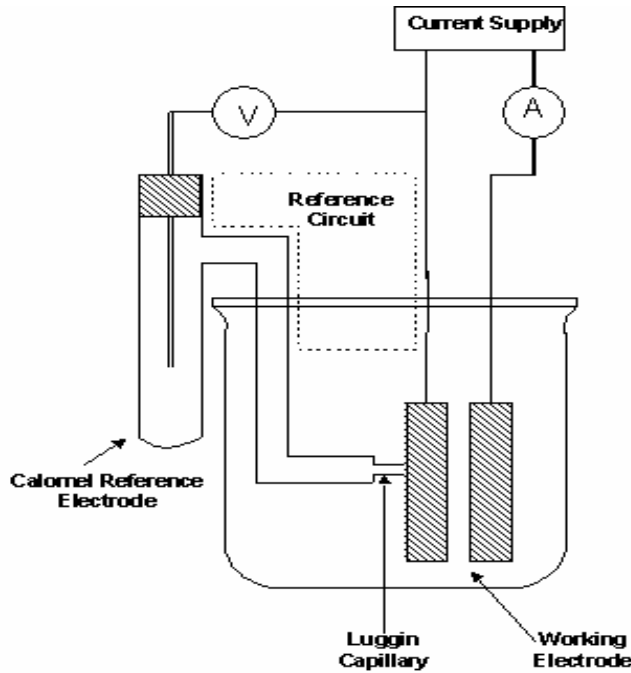


Fig. 5 Experimental setup for measurement of overpotential

Graphs of η v/s $\log i$ are known as Tafel plots (Fig. 6).

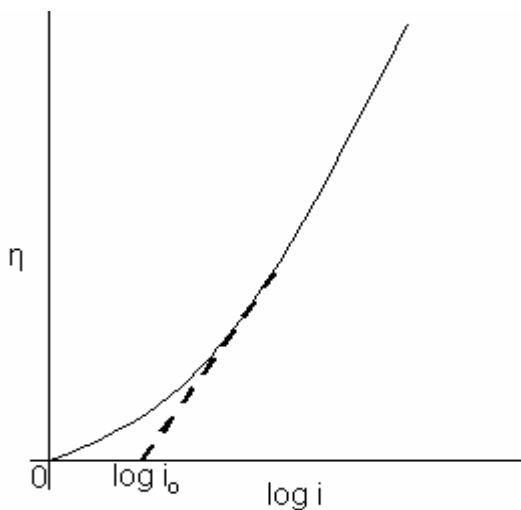
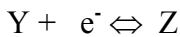
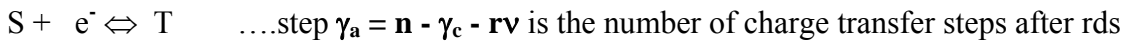
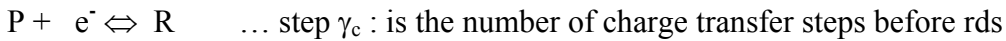


Fig.6 illustrates a typical Tafel plot from which the Tafel parameters i_0 and α can be evaluated. α is obtained as a slope of the linear portion of the Tafel plot and can be

related to the reaction mechanism. On the other hand the magnitude of i_0 is a measure of catalytic efficiency. Usually the Tafel plots for anodic reaction are plotted in positive quadrant. For cathodic reactions these plots are often obtained with current on the negative axis.

iii. Multi-step Reactions

Often electrodic reactions occur in several steps. In multi-step reactions it is important to know the rate determining step (rds). Then it could be possible to predict the nature of the catalyst that would enhance the rds and hence the overall rate of reaction. A multi-step reaction of the type $A + n e^- \leftrightarrow Z$ may be elaborated as shown below



The Butler – Volmer equation for multi-step reaction can be written as

$i = i_0 [e^{\alpha_a \eta^f} - e^{-\alpha_c \eta^f}]$ where α_a and α_c are anodic and cathodic transfer coefficients respectively. $\alpha_a = \gamma_a/v + r - r\beta$ and $\alpha_c = \gamma_c/v + r\beta$. (generally $\beta = 0 - 1$ and $\alpha = 0 - 3$)

B. HYDROGEN EVOLUTION REACTION

Hydrogen is one of the most important chemical which is in high demand in industry as a general purpose fuel, in hydrogenation process, in fuel cells for generation of electricity etc. On commercial scale it is produced by steam reforming of hydrocarbons. Hydrogen thus obtained is not very pure. Although there are several other non – conventional methods to produce H_2 , they are not yet economically viable for large scale production.

i. Electrolysis of water

Very pure hydrogen is produced by electrolysis of water as shown in Fig.7.

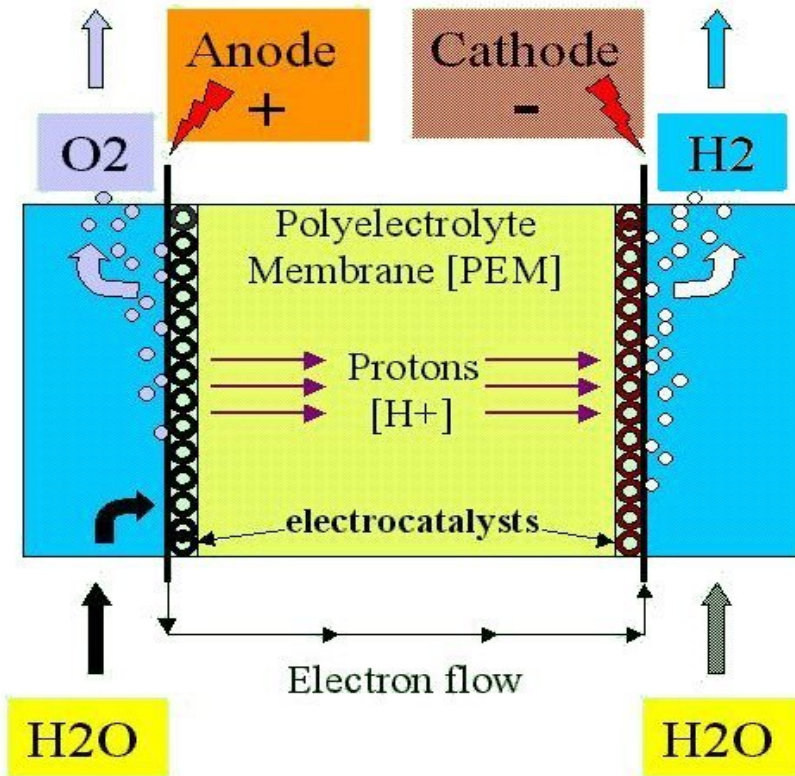


Fig.7: **Some caption is needed for this figure**

The economics of this process can be improved only by efficient electrocatalysis so as to minimize the overpotentials. The applied voltage to produce a given current and hence the desired substance is given by $E_{\text{appl}} = E_e + |\eta_c| + \eta_a + IR$. The significance of this equation is illustrated in Fig.8.

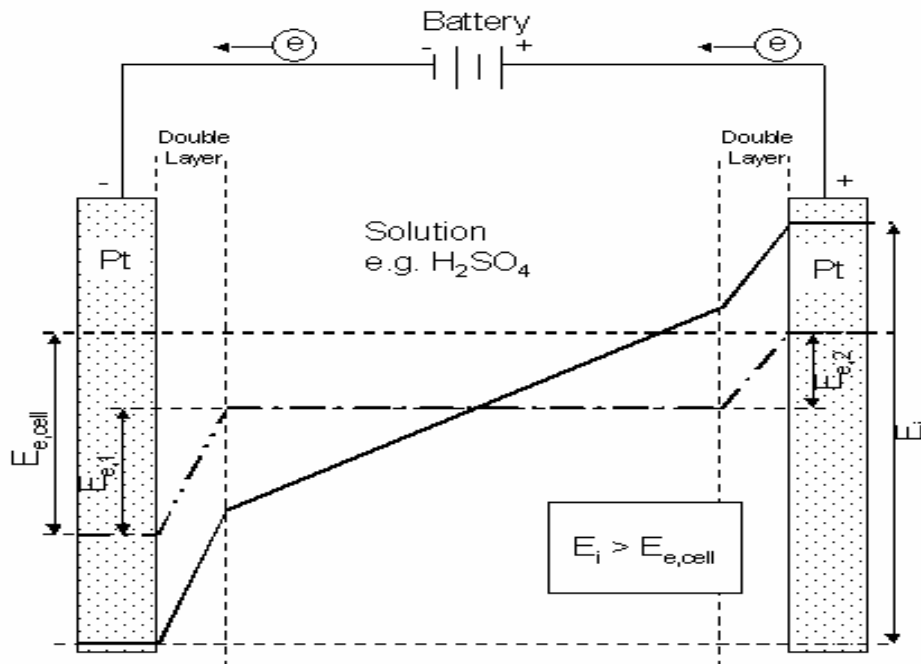


Fig. 8. (**some caption is needed for this figure and the symbols have to be explained**)

Hydrogen is often produced by electrolysis of water between steel cathodes and nickel anodes. Considering the overpotentials and the IR drop, the operating cell voltage is about 2.0 V although the equilibrium cell voltage for decomposition of water is 1.23. A typical cell is known to generate current density of 10^3 A/m^2 and can deliver about $500 \text{ m}^3 \text{ H}_2 \text{ h}^{-1}$.

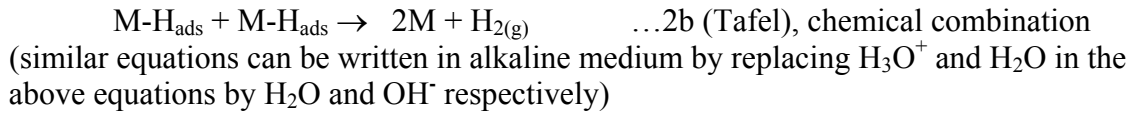
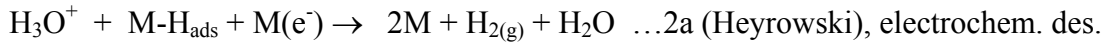
Overpotential for O_2 evolution on nickel is ~ 0.5 volt. It is also a major cause for excessive consumption of electrical energy. If we can replace Ni anode or modify it with an electro-catalytic material so as to reduce the overpotential even by 0.1 volt, the current produced will be more than 10 times the initial value and will cause large overall savings during production of both hydrogen and oxygen from water.

(use eqn. for anodic current $i_a = i_0 e^{\alpha_a \eta^f}$, $\alpha_a = 0.5$ and $\Delta\eta = 0.1$)

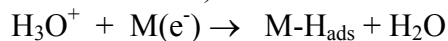
Hydrogen can be produced from acidic as well as alkaline media.

ii. Mechanism of Hydrogen Evolution.

Hydrogen evolution is a multi-step reaction. The following steps are predicted in acidic medium.



Electrode reactions involve electrons and are therefore always quantal i.e they may tunnel to the site before crossing the activation barrier. Whenever an ion in the double layer reaches the Fermi energy level E_F , an electron from the metal E_F tunnels to the ion. (This electron transfer is adiabatic, which means no energy is lost or gained i.e the electron transfer is radiationless). Thus in the reaction,



it is assumed that the electron tunnels to the H – O bonds which have attained appropriate excited vibrational states having energy equal to E_F in the metal. The degree to which this excitation energy exceed the ground state of the reaction is a contribution to the energy of activation E_a .

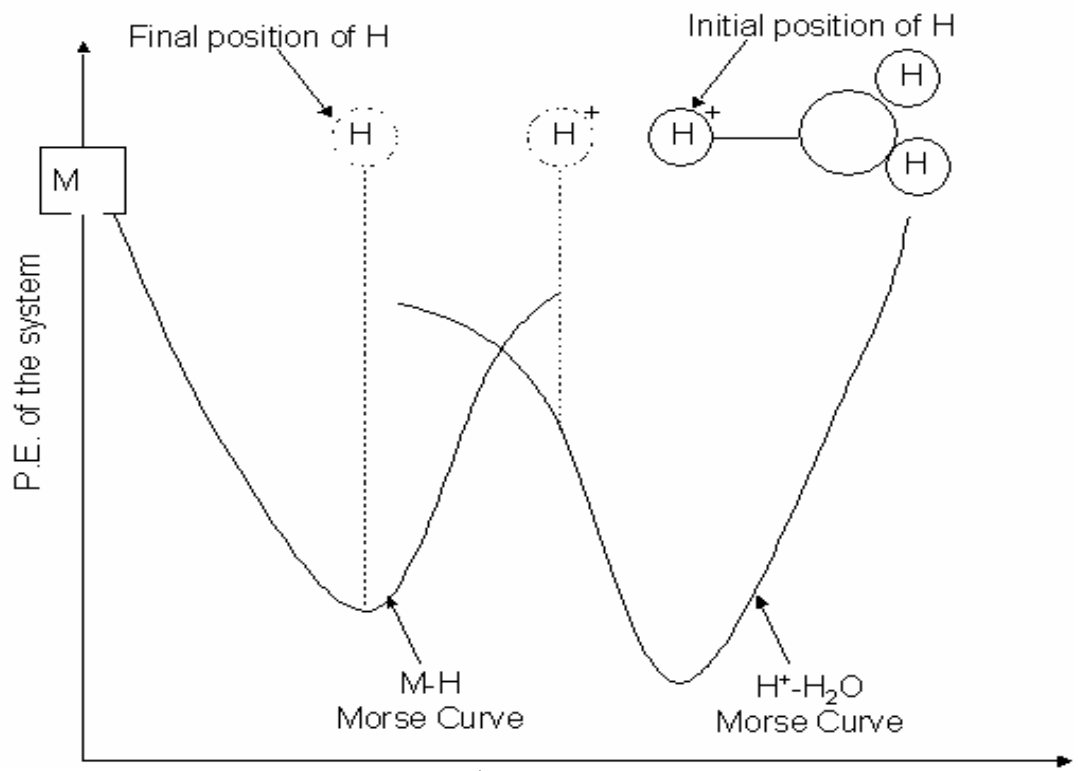


Fig. 9: Position of H atom or (H^+) between M and H_2O

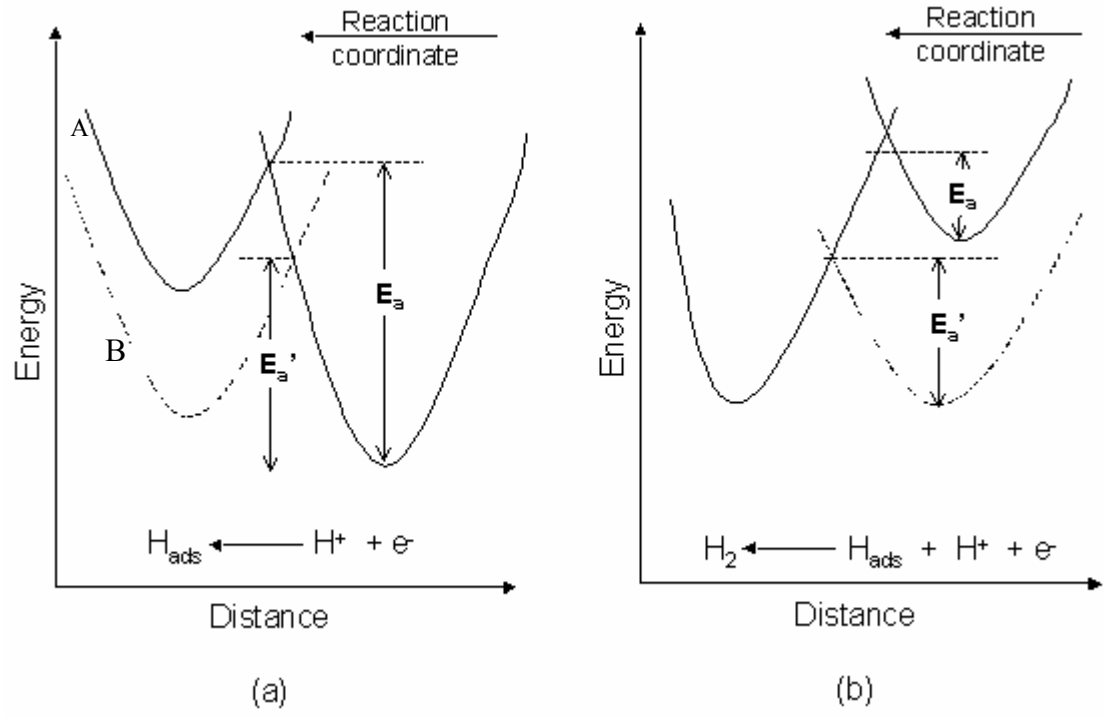


Fig. 10 : Energetics of Electron Transfer during *h.e.r*

Figs. 9 & 10 illustrate the energetics of such an electron transfer. Curve A (Fig.10) is due to the M - H bond vibration. It shifts to lower position as curve B if the energy of

adsorption for M – H is increased. Curve B then intersects the Curve of H⁺ – OH₂ bond (sum of energy of M(e⁻) and energy of H⁺ – OH₂) at a lower level. This decreases the activation energy. It means the H⁺ – OH₂ bond is not necessary to be strained much as higher vibrational states are not required for E_F (metal) to become E_F (solution): a condition required for quantum mechanical tunneling during the formation of M – H bond.

iii. Rate Determining Steps:

The slowest step in a multi-step reaction is known as rate determining step (rds). In a consecutive reaction sequence if the overall reaction is proceeding at a steady state, then all the steps must proceed at the same net rate. This net rate however is controlled by one of the partial reactions. Knowledge of rds is important in electrocatalysis as it gives the idea of the reaction rate if i) potential is changed or ii) if the electrode material is changed.

For the hydrogen evolution reaction we may consider the following two cases to understand the rate determining step, remembering that the Tafel slope $d\eta/d\log i$, often differs characteristically for the rds.

Case 1: The Volmer step.

Let the proton discharge be the rds.

Now for the cathodic process $i = i_0 e^{-\alpha \eta f}$,

which on rearranging becomes $\eta = (1/\alpha f) \ln i_0 - (1/\alpha f) \ln i$

$\therefore d\eta/d\ln i = - (1/\alpha f)$.

If $\alpha = \beta = 0.5$ and changing $\ln i$ to $\log i$, one can write

$$d\eta/d\log i = -2.3 \times 2 \times RT/F = 0.12$$

Thus a Tafel slope of 120 mV/decade would imply a 10 fold increase in current as the potential is made more negative by 120 millivolts. Also an experimental Tafel slope of 120 mV would confirm that the Volmer step is rds.

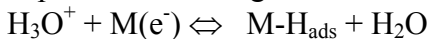
Case 2: Let the hydrogen desorption step be the rds. ($H_{ads} + H_{ads} \rightarrow H_{2(g)}$)

Then the rate of reaction would be proportional to surface coverage.

$$\therefore r = k\theta_H^2 \dots\dots(1)$$

However this being a slow step, excess H_{ads} accumulates on the electrode surface.

A part of H_{ads} then gets reoxidised resulting in the following equilibrium.



Applying Nernst equation for this equilibrium, we get

$$E = E^0 + (1/f) \ln C_{H_3O^+} / \theta_H$$

$$(E - E^0)f = \ln C_{H_3O^+} / \theta_H$$

$$C_{H_3O^+} / \theta_H = e^{(E - E^0)f}$$

$$\theta_H = (C_{H_3O^+}) e^{(E - E^0)f}$$

$$\theta_H = (C_{H_3O^+}) e^{(Ee + \eta - E^0)f}$$

and assuming that E_0 , E_e , f and $C_{H_3O^+}$ are constants, we get $\theta_H = K e^{-\eta f} \dots\dots(2)$

since for cathodic process η is negative, the exponential in eqn.2 is positive.

∴ surface coverage increases with increase in overpotential.

Substituting the value from eqn.2 in eqn.1 we get

$$r = k(K e^{-\eta f})^2$$

and since two electrons are exchanged in the process, the current produced will be given by

$$i = 2F k(K e^{-\eta f})^2$$

$$r = K'(e^{-\eta f})^2$$

$$\ln i = \ln K' - 2\eta f$$

$$\eta = \ln K' / 2f - 1/2f \ln i$$

$$\therefore d\eta / d\ln i = - (1/2f)$$

$$\therefore d\eta / d\log i = - 2.3(1/2f) = - 0.030 \text{ V/dec.}$$

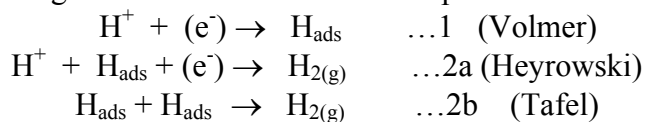
Therefore the current should increase 10 – fold as overpotential is made more negative by only 30 mV.

Thus the Tafel slopes can often be conveniently used to identify reaction mechanisms.

Tafel slopes from the general theory of multi-step reactions:

As mentioned earlier under multi-step reactions, the value of transfer coefficients can be theoretically predicted from the proposed reaction steps. We can then calculate the corresponding Tafel slopes ($\sim 0.059/\alpha$) and compare the same with the specific theory developed for the proposed reactions or compare the values with experimental Tafel slopes. In the instant case one can calculate cathodic transfer coefficient α_c for the various elementary steps involved.

Rewriting the h.e.r mechanism in a simplified form we get,



Case 1: Let the Volmer step above be the rds. Then in the equation. for cathodic transfer coefficient, $\alpha_c = \gamma_c/v + r\beta$, the following values for various parameters can be substituted

$$\gamma_c = 0, \quad v = 1, \quad r = 1, \quad \beta = 1/2. \text{ Thus } \alpha_c = (1 \times 1/2) = 1/2$$

$$\therefore \text{the Tafel slope } d\eta / d\log i = 0.059/\alpha_c = 0.059/0.5 = 0.118 \text{ V} = \sim 120 \text{ mV/dec}$$

Case 2. Let the Tafel step be the rds. For this step

$$\gamma_c = 2, \quad v = 1, \quad r = 0, \quad \beta = 1/2. \text{ Thus } \alpha_c = 2/1 + (0 \times 1/2) = 2$$

$$\therefore \text{the Tafel slope } d\eta / d\log i = 0.059/\alpha_c = 0.059/2 = 0.030 \text{ V} = \sim 30 \text{ mV/dec}$$

Thus the Tafel slopes obtained from the general multi-step reaction theory as well as those obtained by considering the specific h.e.r theory are in excellent agreement. By comparing these values with those obtained by experiment, we can determine the exact rds.

Case 3: Let the Heyrowski step be the rds. For this step

$$\gamma_c = 1, \quad v = 1, \quad r = 1, \quad \beta = 1/2. \text{ Thus } \alpha_c = 1/1 + (1 \times 1/2) = 1.5$$

the Tafel slope $d\eta/d\log i = 0.059/\alpha_c = 0.059/1.5 = 0.040 \text{ V} = \sim 40 \text{ mV/dec}$

In certain cases two different rds may give same Tafel slopes. In such a case, further investigations are necessary to determine the transient species through techniques such as cyclic voltammetry.

iv. Choice of electrocatalysts for h.e.r

It is clear that the hydrogen evolution reaction on a metal depends on formation of $M - H_{\text{ads}}$ bond and its desorption.

If the Volmer step is rds and the Tafel step is fast, then the surface coverage by H_{ads} will be such that $\theta \rightarrow 0$. Conversely if the Volmer step is fast and the Tafel step is slow, then $M - H_{\text{ads}}$ concentration increases and $\theta \rightarrow 1$.

Fig.11 represents the current produced in relation to $M - H_{\text{ads}}$ bond strength on various metals.

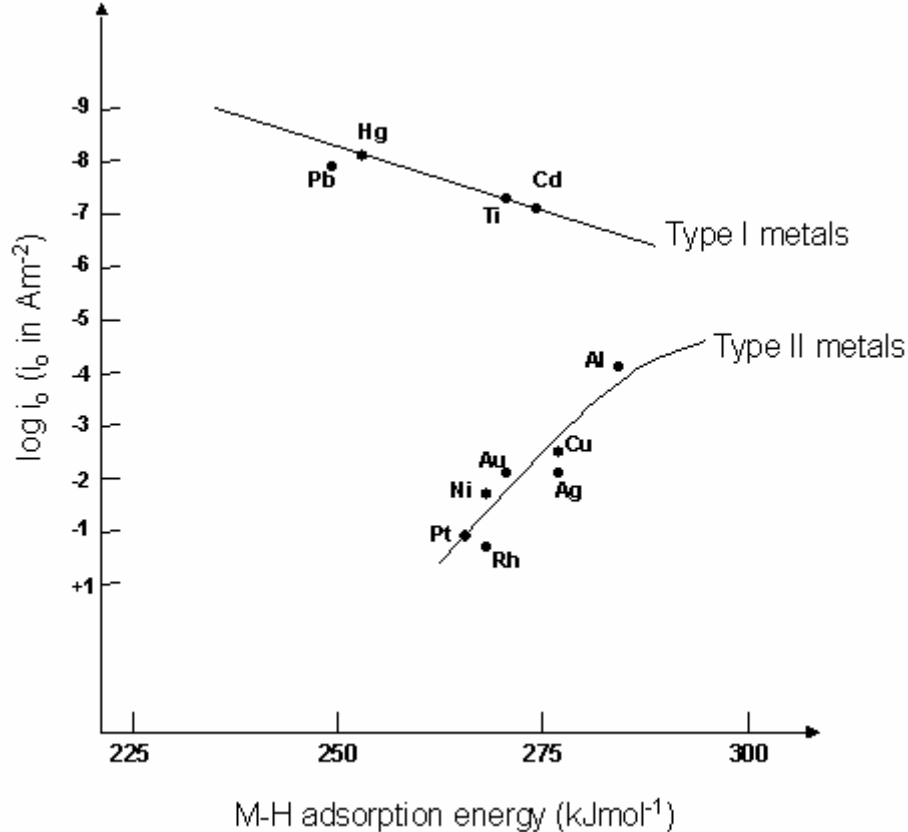


Fig. 11 Activity of various metal electrodes for h.e.r

For Type I metals (e.g. Pb, Hg, Ti, Cd) i_0 increases as $M - H$ adsorption energy increases. The H_{ads} coverage on these metals is very low and is confirmed experimentally. They show low rate of h.e.r and follow mechanism in which the Volmer step is rds.

For Type II metals (e.g. Pt, Ni, Cu, Ag, Au, Mo, Al) i_0 decreases as $M - H$ adsorption energy increases.

The H_{ads} coverage on these metals is very high and can be confirmed experimentally. They generally show high rate of h.e.r and follow mechanism in which the Tafel or Heyrowski step is rds. Often the Heyrowski mechanism is found to operate on these metals. This electrochemical desorption step is slow as it requires that H_{ads} has to be desorbed from the surface by the oncoming proton. This is not easy particularly as $M - H$ adsorption energy increases.

v. Choice of Platinum as electrocatalyst

Graphs of i_0 v/s ϵ_{M-H} give a volcano with Pt near to the peak. (Fig. 11). Pt is therefore often considered as best catalyst. It shows intermediate $M - H$ adsorption energies and highest current. Since desorption occurs relatively faster, the electrode surface is not easily poisoned by adsorbed intermediates. Moreover Pt is stable in acidic medium even at relatively high anodic potentials. Pt though costly, is readily available in various forms(plates, wires, powders)

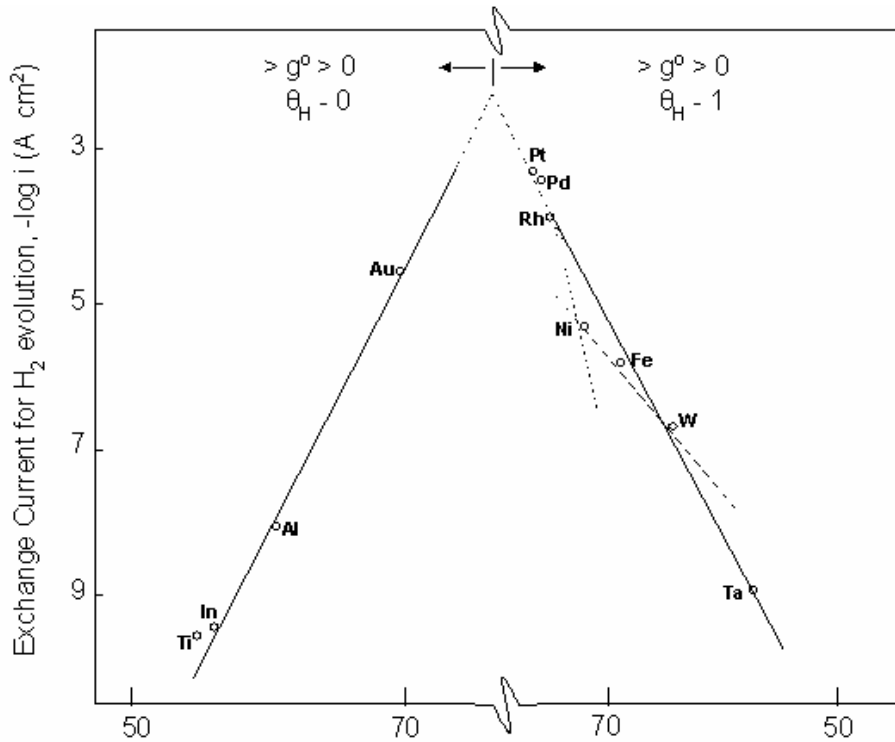


Fig.12. Some caption to this figure is necessary

vi. Comparison of electrocatalytic activity:

The electrocatalytic activity of various materials can be compared by measuring currents produced at a given overpotential. At $\eta = 0$, the values of exchange current densities are used for comparison. Alternatively the activity is compared by finding the overpotentials

required to obtain an acceptable current which may be $\sim 100 \text{ mA/cm}^2$. The material which produces higher current at lower overpotential is generally a better electrocatalyst.

vii. Types of H_{ads} :

Cyclic voltammograms on Pt electrodes in H_2SO_4 solutions exhibit two peaks in the anodic branch as shown in Fig.12.

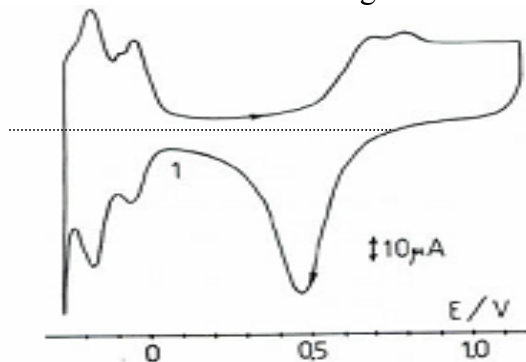


Fig 13. (some caption to this figure is necessary)

a) + 0. 10 V (v/s NHE) , is attributed to weakly adsorbed hydrogen.

b) + 0. 25 V (v/s NHE) , is due to strongly adsorbed hydrogen

These peaks are attributed to adsorption on different crystallographic planes on the surface of Pt which are appropriately oriented to cause adsorption of hydrogen. The electrocatalytic activity would then depend upon the preferred orientation concentration of the crystal planes. Sometimes a third peak could be observed due to adsorption of bisulphate ion.

C. ELECTROCATALYSIS IN FUEL CELLS

i. Principle of a $H_2 - O_2$ fuel cell

Major applications of electrocatalysts today apart from water electrolysis, are in oxygen reduction reactions in fuel cells and air batteries as well as for anodic oxidation of fuels in fuel cells. Fuel Cell is an environmentally friendly and energy efficient power source. It converts chemical energy stored inside the fuel into electrical energy without any SO_x or NO_x emissions. The fuels such as H_2 , CH_3OH etc. are electrochemically oxidised in presence of air or O_2 .

Fuel Cell is a 19th century invention (1839) of William Grove. However a fuel cell that could produce significant energy (5 kw) was developed only in 1959 by F.T. Bacon. Bacons alkaline fuel cell led NASA to design fuel cells that would later power the Apollo and Gemini spacecrafts in 1969 and early 70s.

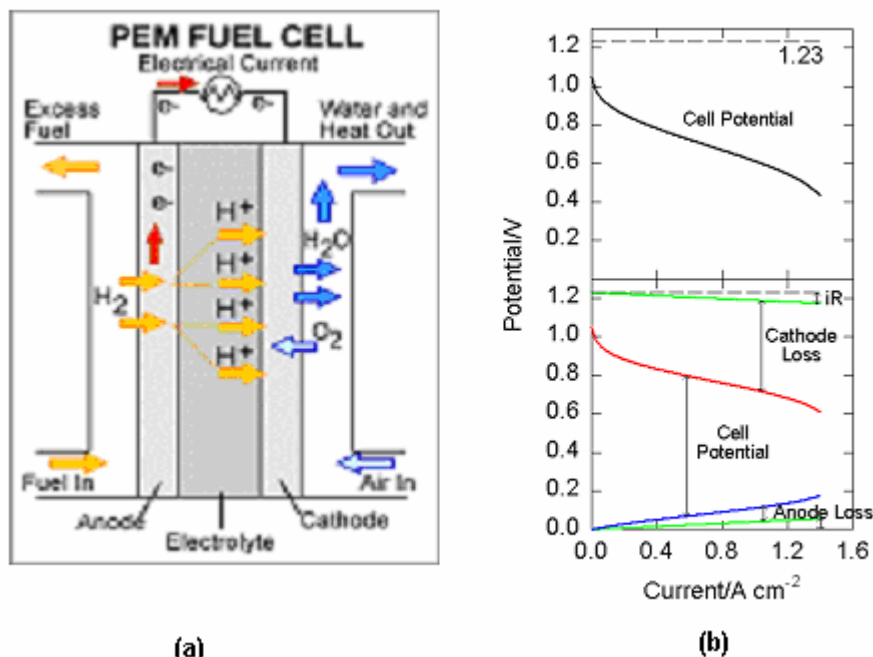


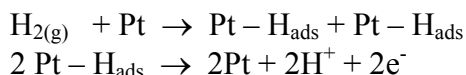
Fig. 14.(a) illustrates working of a H₂ – O₂ (PEM) fuel cell.
 [reproduced from <http://www.eere.energy.gov/hydrogenandfuelcells/fuelcells/types.html>]

Theoretical potential of a hydrogen – oxygen fuel cell is 1.23 volt. However mainly due to overpotential losses at the anode and cathode, the potential drops as illustrated in the Fig 14 (b).

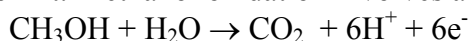
Hence to make fuel cells economically viable, it is imperative to minimize the overpotential losses by appropriate electrocatalysis. Pt is by far the best electrocatalyst both for anodic as well as for cathodic reactions in these fuel cells. Efficient electrocatalysis would involve designing of suitable electrodes for efficient utilization of Pt or its more cheaper substitutes provided the latter are almost as stable and have reasonably high activity.

ii. Catalysts for H₂ and methanol oxidation

Kinetics of oxidation of pure H₂ is quite facile on Pt electrocatalysts. In this, H₂ undergoes dissociative adsorption on Pt sites followed by dissociation of the adsorbed H atoms.



However when H₂ is replaced by methanol as a fuel, the oxidation kinetics is poor even on Pt. Methanol oxidation involves an overall release of six electrons



and is initially associated by stepwise dehydrogenation of protons resulting most often in formation of a Pt – CO type adsorbed intermediate (Fig 15).

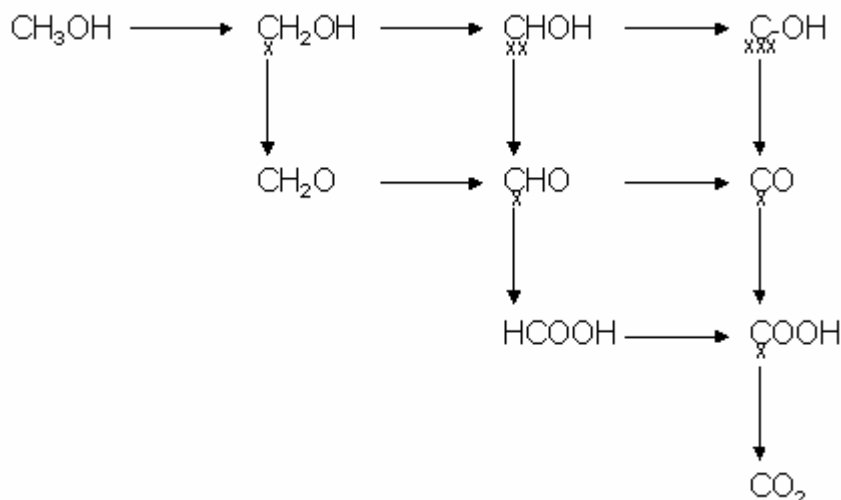


Fig. 15 Reaction scheme for methanol oxidation

The dehydrogenation occurs in the direction from left to right and oxidation by adsorbed OH_{ads} occurs in the perpendicular direction.

Any catalyst component which directly or indirectly assist decomposition of Pt – CO_{ads} into CO_{2(g)} would result in more efficient catalysis. One of the best catalysts so far for methanol oxidation is Pt – Ru bimetallic. The second component such as Ru being more oxophilic than Pt, results in more efficient decomposition of water to form Ru – OH_{ads} type species (such a species may also be formed by adsorption of hydroxide ions from solution). The latter species then facilitates decomposition of CO_{ads} into CO_{2(g)}. The activity of the Pt based catalysts are further enhanced by using ternary and quaternary solid alloys involving elements such as Sn, Ni, Cr, Mo, W, Os etc. The current trend is also to investigate newer support materials such as use of mesoporous carbons or zeolite/carbon composites, conducting polymers or base metal oxides both as supports or promoters to observe synergistic effects. Nature of support and the methods of dispersing the active components on the supports in nanosize dimensions and designing of electrodes to provide efficient pathways for transport of active materials is crucial for efficient electrocatalysis.

iii. Catalysts for Oxygen Reduction:

The oxygen reduction reaction (ORR) can proceed by two overall pathways,

- i. a direct 4-electron pathway and
- ii. an indirect 2-electron pathway.

The direct 4-electron pathway is preferable as it does not involve peroxide species in solution and the Faradaic efficiency of the reaction is greater.

Some of the possible intermediates during oxygen reduction in acidic electrolytes may be considered to be formed as shown below

- i) $O_{2(g)} \rightarrow O_2^*$
- ii) $O_2^* \rightarrow O_{2(ads)}$
- iii) $O_{2(ads)} + e^- \rightarrow O_2^-$
- iv) $O_2^- + H^+ + e^- \rightarrow HO_2^-$



Because of the complexity of the reaction and difficulties in the breaking of O – O bond, the electrode kinetics is very poor. The adsorption of an oxygen species on the surface of the metal particles is necessary for electron transfer.

The reduction kinetics are known to be greatly influenced by

- i. the extent of Pt loading as well as particle size (a particle size of ~ 5nm is believed to be optimum)
- ii. geometry, crystal structure and d – band vacancy of the metal crystal.
- iii. thermal or electrochemical activation of the electrodes

Pt/C electrodes are known to be most active for the ORR. Substitute catalysts being investigated include

- i. metal oxides particularly those having spinel and perovskite structures
- ii. transition metal macrocycles such as Fe or Co phthalocyanins and porphyrins which could assist in O – O bond cleavage

iii. Porous Electrodes

Porous gas diffusion electrodes (*pgde*) provide enhanced electrochemically active surface areas for efficient electrodic reactions.

Power of a fuel cell is given by the equation $P = I \times E$ where $E = E_c - |\eta_c| - \eta_a - IR$. Thus the power would decrease due to overpotential losses. It can be shown that these losses can be minimized by increasing the active surface area. The limiting current density increases by more than 10^4 times that on planar electrodes. Fig. 16 illustrates gas diffusion paths through a porous electrode filled with electrolyte solution.

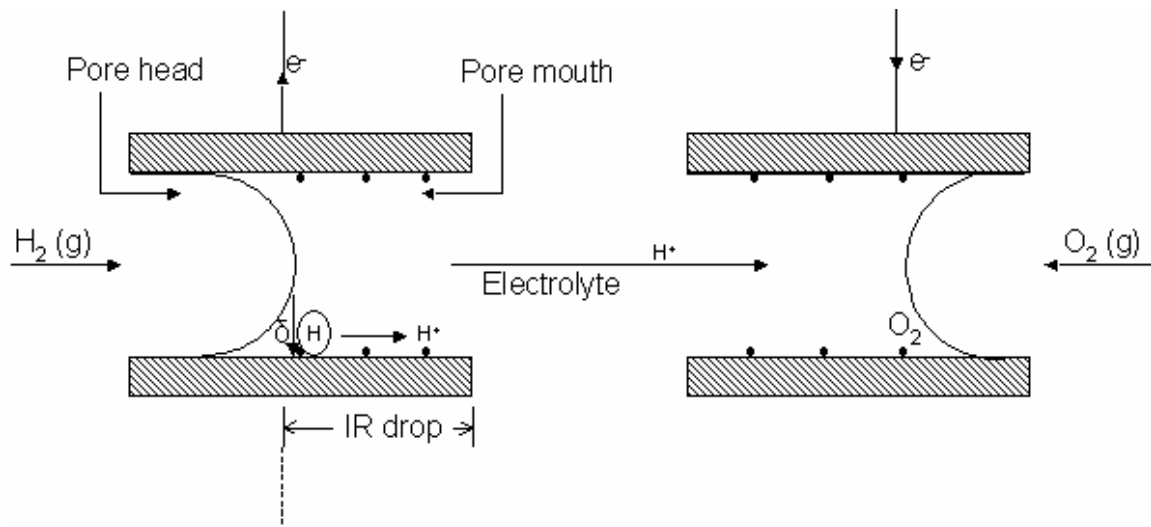


Fig. 16: Gas diffusion through pores of a porous electrodes used in fuel cells

But the following drawback associated with such pores in the electrodes have to be considered.

- a) pores waste electrical energy due to IR drop across the length of the pore

- b) lack of available reactant molecules which decrease as one goes from head to mouth of the pore.

The above difficulties can be largely overcome by using polymer electrolyte membranes such as Nafion which is an efficient protonic conductor.

The main prerequisite of a good *pgde* is a 3 – phase contact between the gas supply, the catalyst particle and the electrolyte. Fig. 17 gives a cross – section of such an electrode.

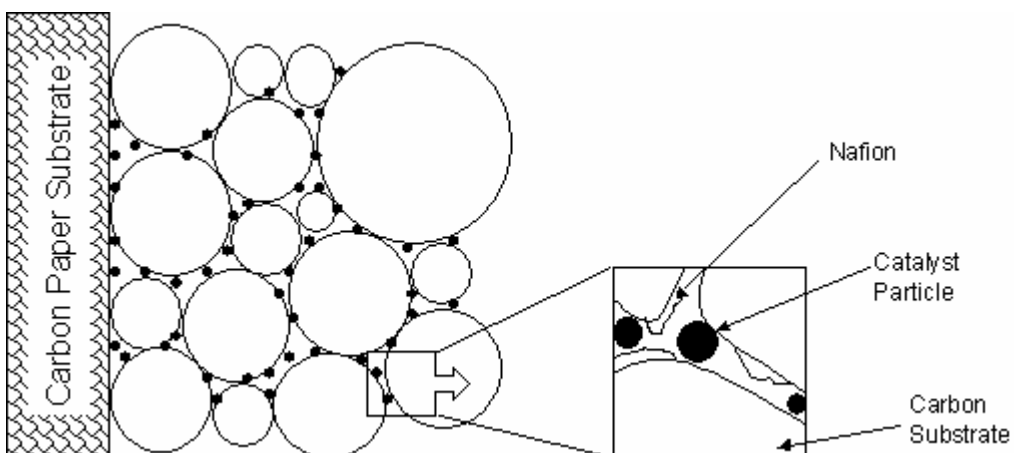


Fig. 17 The cross section of a porous electrode showing the three phase boundary

The catalyst particles must be in direct contact with an electronic conductor to ensure that the electrons are supplied to or taken away from the reaction site. Electronic conductivity is provided by a carbon support onto which the catalyst particles are supported. The three-phase boundary is made by impregnating the catalyst/support powder with some ionomeric binder (usually Nafion solution) before pressing the electrode onto the membrane. This ensures good contact of most catalyst particles with ionomer material. Gas diffusion occurs through the backing layer and the carbon support to the catalyst particles. When using humidified gases or methanol/water mixture the catalyst layer must be sufficiently hydrophobic to prevent the pores from flooding. This hydrophobicity can be provided by introducing PTFE as a binder in combination with Nafion which is hydrophilic. Usually the catalyst is made into an ink with water and isopropanol and mixed with a binder material (the optimum binder quantity depends on the type of catalyst) after which the ink can be applied onto the membrane.

The pore architecture is important for providing multiple gas diffusion paths so that the gas can get adsorbed over as much possible catalyst active sites. Diffusion of small molecules through micropores such as that in zeolites (< 2 nm) can exhibit hindered molecular transport. The transport of small molecules in media featuring large mesopores (>10nm) and macropores (>50 nm) can approach rates of diffusion comparable to those in open medium. Mesoporous nanostructure in which pore and solid structure components are controlled at nanoscale level such as through surfactant templated synthesis which create periodic porosity often cause plumbing problem: (periodic porosity being one dimensional and nanoscopic, any internal blockage shuts off the

catalysed walls of that capillary pore from the reaction site. 3D mesoporous architecture with continuous and aperiodic porous networks that wrap around the catalytic solid network offer transport routes around blockages; such architecture could be obtained through methods such as sol – gel derived ultraporous aerogels[9].

D. ELECTROSYNTHESIS

Most of the chemical synthesis involves oxidation or reduction reactions and electrons are cleanest reagents for such reactions.

i. Principle

Whether a substance can be electrochemically oxidized by O_2 or reduced by H_2 will depend on the Nernst potentials (their placement on emf series in relation to hydrogen and oxygen – the electrochemical series is pictorially shown in Fig.18)

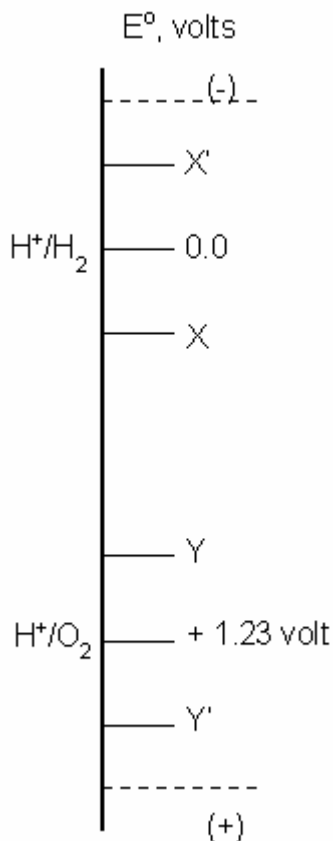


Fig. 18: Potential of the electroactive species in relation to position of H_2 and O_2 in the electrochemical series

Consider species X and Y taken for electrochemical reaction. In aqueous medium X can undergo reduction by gain of electrons from H. But X' which is above H in the emf series will not undergo reduction by H. To cause reduction of X' , we have to supply electrons to it from an external source. But this can cause preferential reduction of H^+ as H is below X' . Therefore H_2 gas will be evolved. Therefore for

reduction of X' we must choose electrodes having overpotential higher than the reversible potential of X'. Such an electrode could preferably be of Hg, as H₂ overpotential on Hg is ~ -1.2 V.

Similarly O₂ can cause oxidation of Y and not Y'. To oxidize Y' the reaction will have to be carried out at a high enough positive electrode potential and yet should not cause oxygen evolution. Such an electrode could be PbO₂, as oxygen overpotential for it is ~ + 2.0 volt. Thus Hg and PbO₂ electrodes cause a potential window in the range -1.2 to + 2.0 V for safe electrosynthesis in aqueous media.

To avoid difficulties caused by H₂ or O₂ evolution, often electrosynthesis is carried out under certain conditions under non-aqueous media or in molten electrolytes as solvents e.g. (AlCl₃ + NaCl) is molten at 180 °C and is a safe electrosynthesis medium for many reactions.

Electrosynthesis in many cases can have advantages over conventional chemical synthesis such as

1. It is convenient to supply more energy electrochemically.
2. Reactions can be more selective at electrodes by precisely controlling applied potentials.
3. Innovative chemical synthesis is readily possible by changing nature of electrodes.
4. Application of potential can cause decrease in activation energy and permit reactions at much lower temperatures.

The main disadvantage could be the high cost of electrical energy and should be decided in relation to the cost of materials produced.

ii. Applications.

The following scheme (Fig. 19) illustrates the dependence of electrosynthesis products on the nature of the electrode.

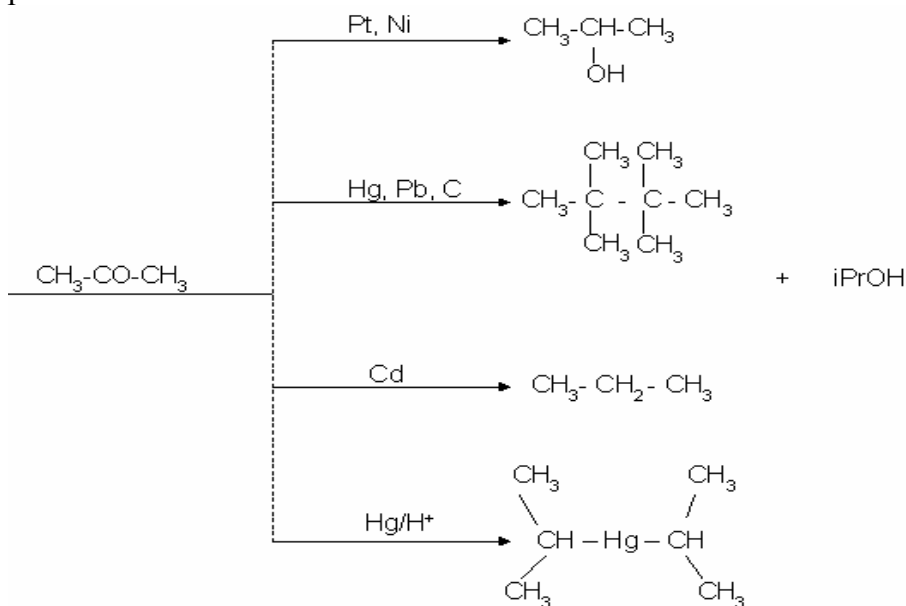
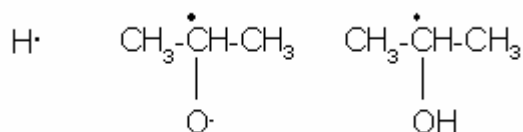


Fig. 19: dependence of electrosynthesis products on the nature of the electrode.

Some of the electrogenerated species were



Electrosynthesis is used in commercial manufacture of several industrially important compounds eg.

1. Cathodic reduction: Large scale manufacture of adiponitrile is done by the cathodic reduction of acrylonitrile.
2. Anodic oxidation: A good example of anodic oxidation is the oxidation of carboxylic acids to form a range of organic compounds. The nature of the compounds depends on the nature of electrode (e.g.Pt or C), electrode potential and electrolyte composition (Kolbe's synthesis). The products are assumed to be formed via free radical/carbonium ion intermediate. The following compounds can be obtained during electrolysis of sodium propionate using Pt or carbon electrodes.

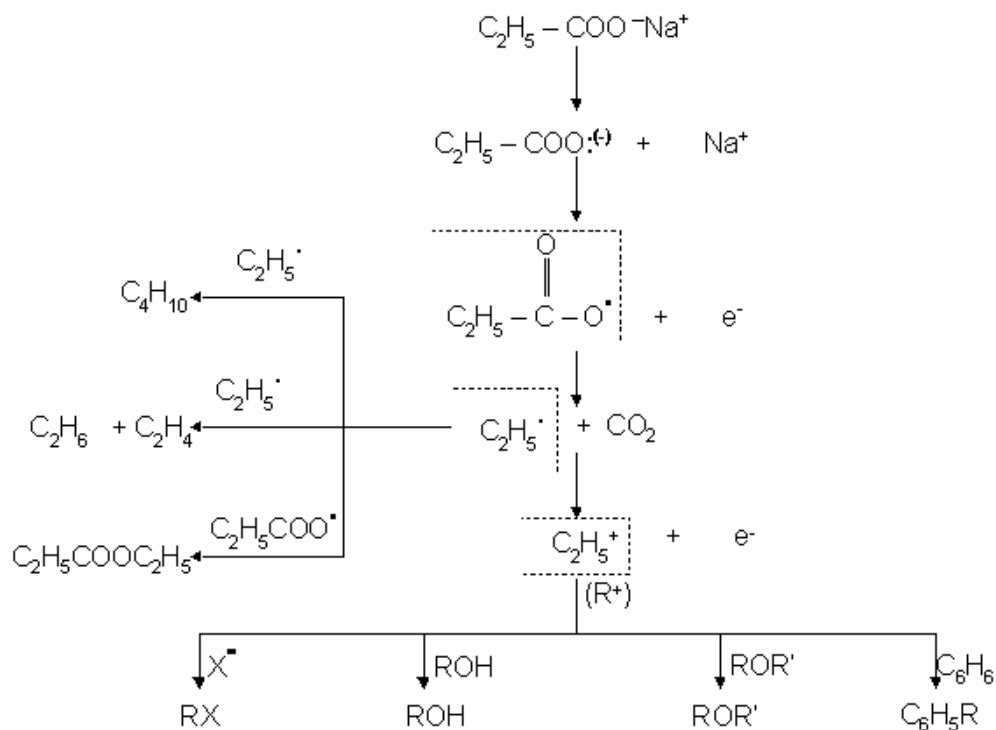


Fig.20: Electrosynthesis of useful organic products by Kolbe's method

Electrocatalytic oxidation can also be carried out using electrogenerated species such as oxidative dimethoxylation of furan by Br^+ electrophile generated *in situ* from Br^- .

iii. Special features of electrocatalysis as compared to conventional electrocatalysis

1. The effect of electric field: the rate may change by several orders of magnitude with increasing over potential.
2. Reactivity at low temperatures: Electrocatalysis occurs at much lower temperatures than conventional heterogeneous catalysis.
3. Activation of catalyst: Certain electrode materials can be activated either before or during an electrode reaction so as to produce an increased reaction rate i.e. a higher current density at same constant value of over potential.

Activation can be achieved in several ways. e.g.

- (a) By application of alternate anodic and cathodic pulses by which fresh, clean (oxide free) electrode surfaces are produced.
 - (b) By application of ultrasonic radiation.
4. Increasing the power output by changing the reaction pathway eg reduction of O_2 is a slow process at a given electrode. The reduction rate can be enhanced by using a suitable redox system.
 5. The use of porous electrodes: When porous electrodes are used diffusion overpotentials are practically eliminated by minimizing the thickness of the diffusion layer δ instead of the costly stirring process. Since δ is very small for porous electrode the limiting current is very high.
 6. Chemical modification of electrodes: It is deliberate and continuous modification of electrode surface to produce electrodes with new and interesting properties that may form the basis of new applications of electrochemistry and novel devices. This can be done by several methods such as
 - (a) Strong chemisorption: eg. organic species such as those containing double bonds are hydrophobic and strongly adsorb from aqueous solutions on carbon or Pt surfaces .
 - (b) Covalent attachment: eg. oxidized carbon or metal electrodes are silanized and is further treated with a suitable compound so that a desired group can be attached.
 - (c) Polymer layers: by dipping the electrode into a solution containing a dissolved polymer eg. poly(vinylferrocene) and allow the solvent to evaporate to form thin films on the surface. Thin polymer films can also be made by dip coating or spin coating.

E. EXERCISE

1. The exchange current density for the evolution of H_2 on Pt is 0.8 mA/cm^2 . What is the current density at 27°C for an overpotential of 2.0 mV ?
2. The following data were obtained for the evolution of H_2 from H_2SO_4 at 25°C . Determine the value of the transfer coefficient.

$-\eta/(\text{mV})$:	0.03	0.09	0.11	0.16	0.19	0.30
$i/\text{mA/cm}^2$:	0.74	2.77	3.79	8.31	13.3	21.1
3. from the current versus voltage data below calculate the value of the symmetry factor β for the reduction of Fe^{3+} : $T = 298 \text{ K}$ and $OCV = 0.75\text{V}$

V/(V)	0.70	0.65	0.60	0.55	0.50
I/(mA)	4.30	12.20	27.00	64.20	144.00

4. The following measurements were made at $T = 298$ K of current i as a function of η in a cell where the electrode was made positive

$i/10^{-5}$ A	15.9	25.4	164.3	1063.4
$\eta/10^{-3}$ V	75	100	200	300

How far are these data consistent with the simple expression, and what value of α do they predict? Do you expect this equation to work at values of η of around 10 mV?

5. The following $i - \eta$ data for the evolution of hydrogen on a metal at 300 K have been obtained:

$i/\text{A cm}^{-2}$	-10^{-4}	-5×10^{-4}	-2.5×10^{-3}	-10^{-2}
η/V	-0.010	-0.031	-0.052	-0.070

Which of the three mechanisms is illustrated by the above data? Take $f = 0.0258$ V.

6. The exchange current densities for the hydrogen evolution reaction in 1 mol dm^{-3} acid and the strengths, $E_{\text{M-H}}$, of the corresponding M-H bonds are given for a number of metals in the table below.

Metal	Zn	Ni	Pt	W	Ti
$i_0/(\text{A/cm}^2)$	1×10^{-10}	3×10^{-8}	10^{-5}	10^{-9}	10^{-11}
$E_{\text{M-H}}/\text{KJmol}^{-1}$	8	12	15	18	20

To what extent are these data qualitatively consistent with the mechanism predicted in Q4 above?

7. How long will it take for a current of 0.2 A to deposit 0.3 g of Ag (at. mass = 108) on the basis of 90% current efficiency?

8(a). What volume of H_2 gas at STP will be produced during electrolysis of water by passing current of 0.01 mA/cm^2 between Pt electrodes of area 1 m^2 .
(neglect the effect of overpotentials)

(b) What will be the efficiency of the process if the ohmic drop is 0.5 V and the anodic and cathodic overpotentials are 0.01 and 0.40 respectively?

9. Refer C(iii) wherein five possible elementary steps are predicted for the ORR. If the observed transfer coefficients are $3/2$ each, predict the possible rate determining step.

10. Following CV profile have been observed on Pt electrode in 1 mol/dm^3 H_2SO_4 solution. Interpret the various features of the profile and explain how the electrochemical surface area could be determined.

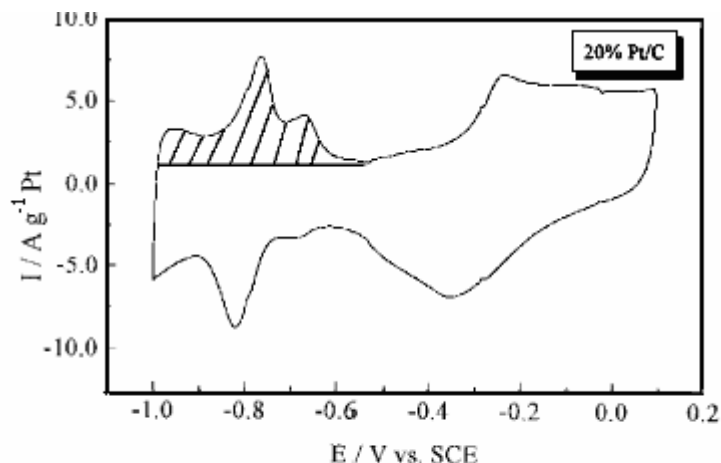


Fig. 21 Cyclic voltammogram of a 20 % Pt/C electrode at 25 °C in 0.5 M H₂SO₄ at a scan rate of 10 mV/s

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