

# **BASIC ELECTROCHEMISTRY FOR THE STUDY OF FUEL CELLS**

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## **1. Introduction**

The performance of a fuel cell is determined by the kinetics of the reactions occurring at the electrode and by the transport of reactants through the solution and in the electrode. It is to be noted that the ideal or maximum efficiency of any electrochemical energy converter depends upon electrochemical thermodynamics whereas the realizable efficiency depends on electrode kinetics. The fact that the real efficiencies are less than the ideal efficiencies inculcates interest in understanding the fundamental theory governing this direct electrochemical conversion of chemical energy to electricity. Further, in fuel cells applications, the power per unit weight as well as the efficiency are important factors to be considered. Since power is the rate of producing energy, the kinetics of the electricity producing interfacial charge transfer reactions, i.e., electrode kinetics becomes important. For an electrochemical energy converter working ideally, it has been shown that the free-energy change of the electrochemical reaction may be converted totally into electrical energy. Thus, an electrochemical energy converter has an intrinsic maximum efficiency given by

$$\epsilon_i = \Delta G / \Delta H = 1 - (T\Delta S / \Delta H) \quad (1)$$

It is perhaps not appropriate to regard this equation as indicative of an intrinsic maximum efficiency of less than 100 percent since there is a possibility that in some reactions  $\Delta G$  can exceed  $\Delta H$ . Over potential losses reduce the practical efficiencies of fuel cells to values less than the intrinsic maximum efficiencies. However, when sufficient advances in electrocatalysis are made (thereby reducing over-potential) it might be possible to attain practical efficiencies and close to maximum intrinsic efficiencies, particularly in situations where the power density does not have to be high, so that the current density and hence over potential can be low. Useful work (electrical energy) is derived from a fuel cell only when a reasonably large current is drawn and as a consequence the cell potential will be decreased from its equilibrium potential due to irreversible losses. The losses in galvanic elements

under the conditions of delivering current have been termed 'polarization' and this expression implies a multitude of phenomena, which are related to the kinetics of the electrode reactions. Polarization is influenced by the ionic mobility of the reaction partners (thermodynamic equilibrium) and even responsive to the factors of the cell design - for example, the dependence of *cell resistance* or the *geometrical shape* of the electrodes.

"Polarization" is also termed as "over voltage or over potential". In a practical view point, the "over voltage" is the voltage difference that is measured between the "open circuit voltage" and the "terminal voltage" under the conditions of current flowing in either directions. The terminal voltage is also termed as "closed circuit voltage". During discharge process, the terminal voltage is lower and while charging, the terminal voltage is higher than the open circuit voltage. The "over voltage" can be considered to be a measurable value for the losses appearing as a result of the current flow in either direction. Thus, the over potential implies "the potential of the electrode when a net current flows through the electrode ( $i \neq 0$ ) diminished by the equilibrium potential (when  $i = 0$ )". The characteristic response of a fuel cell is measured in terms of a polarization curve and a typical one that is normally observed is given in Fig.1.

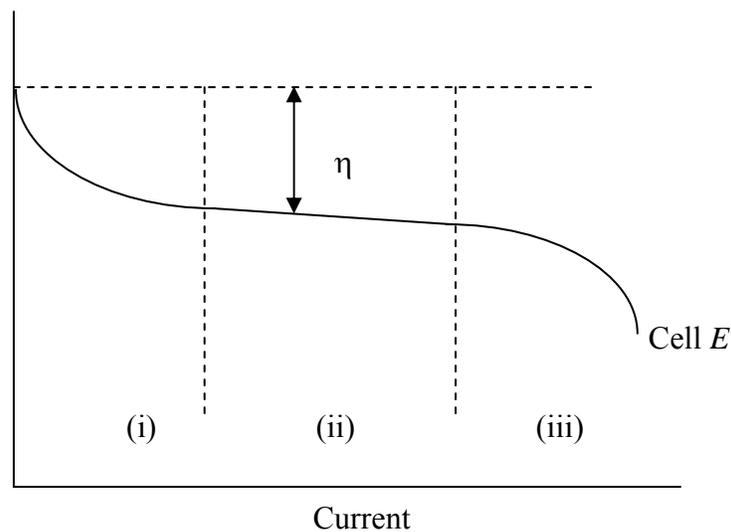


Fig. 1. Typical polarization curve for a fuel cell: voltage drops due to: (i) surface reaction kinetics; (ii) electrolyte resistance; and (iii) reactant/product diffusion rates.

## 2. Electrode – Electrolyte Interface

### 2.1. Equilibrium at an Electrode

The equilibrium that exist at an electrode/electrolyte interface can be understood by dipping a metal electrode in a solution of its ions like a Zn rod in a solution containing  $Zn^{2+}$  ions. The situation existing existing in an electrode at equilibrium is shown in Fig.2.

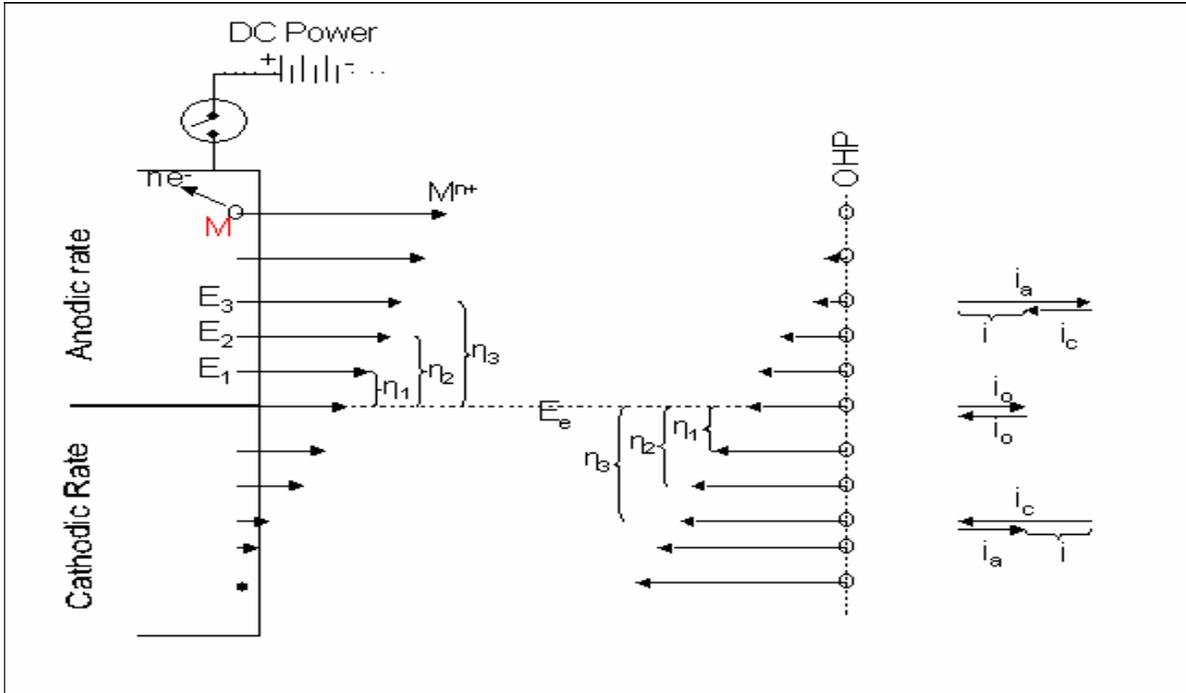


Fig.2. Equilibrium of the type  $M(s) \leftrightarrow M^{n+} + n e^-$  (e.g.  $Zn(s) \leftrightarrow Zn^{2+} + 2e^-$ ) existing at the electrode/electrolyte interface.

At a certain stage, the two rates ( anodic and cathodic rates) become equal and equilibrium is established at the electrode. The potential acquired by the electrode at equilibrium is known as equilibrium potential  $E_e$ . Over potential is then the departure of electrode potential from its equilibrium value and is 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  $i_o$  for an electrode of unit area. Net anodic or cathodic currents can be obtained by applying suitable over potentials. 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. The schematic representation of electrode/electrolyte interface is shown in Fig.3.

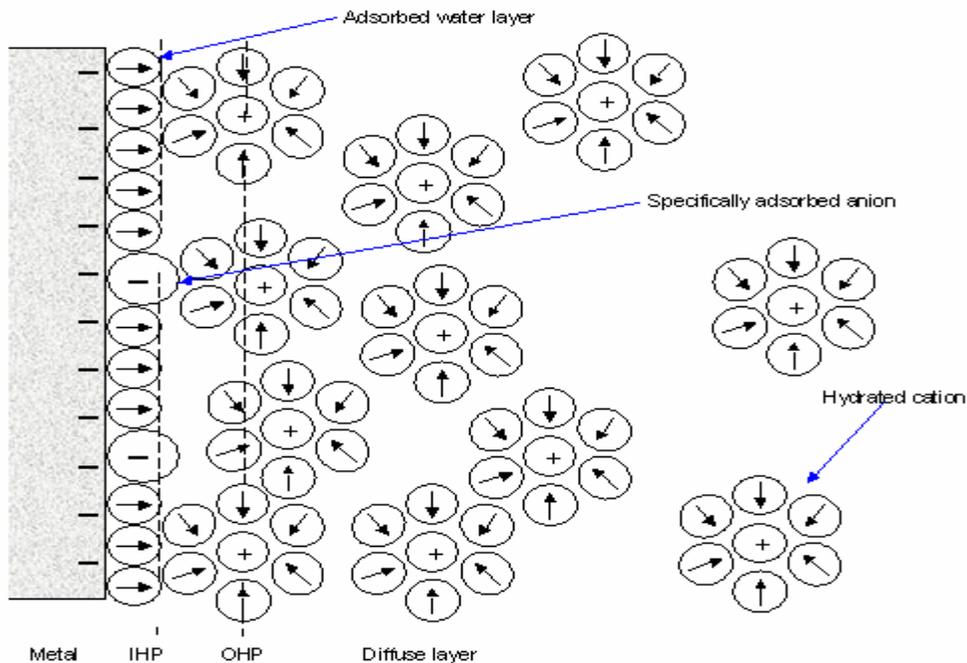


Fig.3. The schematic representation of an electrode/electrolyte interface; IHP and OHP stand for Inner and Outer Helmholtz Plane.

## 2.2. Charge (electron) Transfer at Electrode/Electrolyte Interface

The electron transfer at the electrode/electrolyte interface depends on the relative positions of the Fermi level and the highest occupied and lowest unoccupied orbital of the substrate undergoing the charge transfer. During this charge transfer, if the potential of the working electrode is controlled then the electrons transferred to the electrode is drained off as current through the cell and the opposite would occur at the counter electrode. A pictorial representation of this is shown in Fig.4.

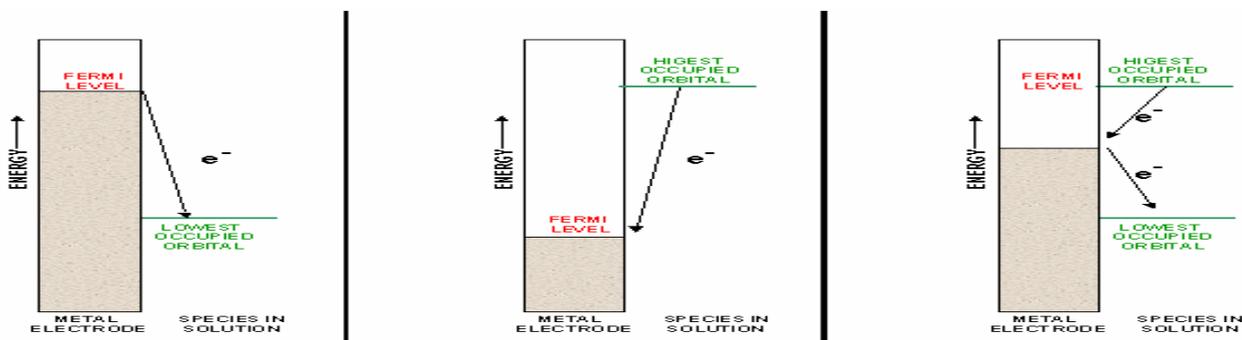


Fig. 4 Charge transfer energetics at a metal electrode/electrolyte interface

### 2.3. Current – Potential Relationships

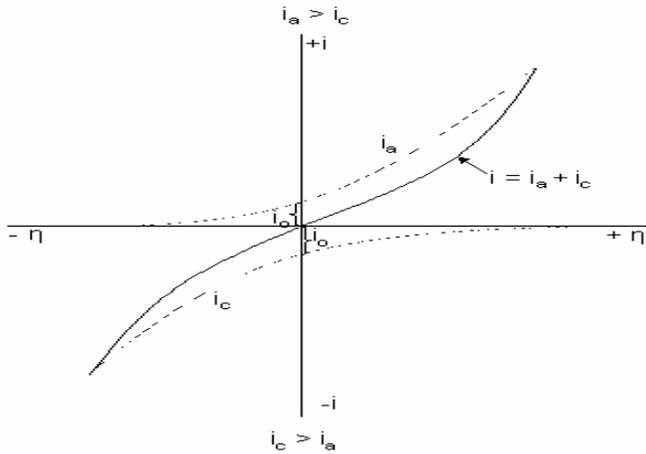
It is therefore necessary to understand current –potential relationships under various conditions. Under equilibrium conditions when the net current flowing is equal to zero, the cell potential is given by the Nernst equation. Typical form of Nernst equation is given as

$$E = E^{0i} - (RT/nF) \ln \{ C_R^s / C_O^s \} \text{ ----- (2)}$$

Where E is the electrode potential and  $E^{0i}$  is the conditional or formal potential and  $C_R$  and  $C_O$  refer to the concentration of the reduced and oxidized species in solution. Another equation of interest for Fuel cell applications is the Butler-Volmer equation. It is given by

$$i = i_0 [ e^{(1-\alpha)\eta f} - e^{-\alpha\eta f} ] \text{ .....( 3 )}$$

where  $\alpha$  is known as transfer coefficient,  $\eta$  is over potential and  $f = F/RT$ . For one electron transfer reaction often symbol  $\beta$  is used in place of  $\alpha$ .  $\beta$  is known as symmetry factor. Both  $\beta$  or  $\alpha$  combine with over potential to determine the magnitude of electrical energy supplied to the electrode to obtain the desired current. The terms in equation 3 are illustrated graphically in Fig.5.



**Fig.5.** Graphical representation of the Butler - Volmer equation

A plot of  $\eta$  versus  $\log(i)$  is known as Tafel plot. Fig.6 illustrates a typical Tafel plot from which the Tafel parameters  $i_0$  and  $\alpha$  can be evaluated.  $\alpha$  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.

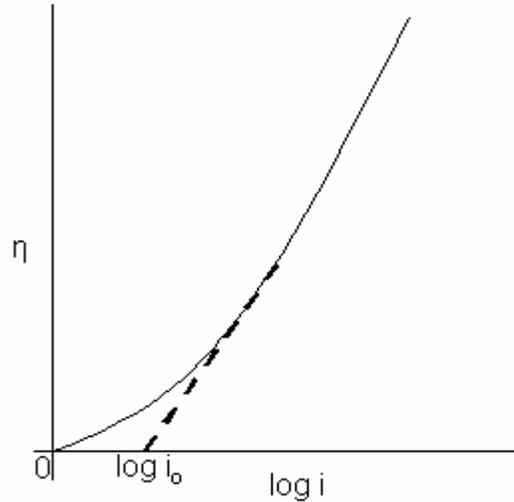


Fig.6 A typical plot of  $\eta$  versus  $\log(i)$  usually known as Tafel Plot.

#### 2.4. Models of Electrode – Electrolyte Interface

There are various models to describe the details of the electrode-electrolyte interface. All these models stem from the concept that there is a double layer existing at the interface and the dynamics of the electron transfer process is controlled by the potential difference present between these two layers. However, there are subtle differences between each of the models and a brief description of each of these models is given.

The first double layer model due to Helmholtz, considered the ordering of positive and negative charges in a rigid fashion on both sides of the interface, (double layer or compact layer), the interactions not extending any further into the solution side. This situation similar to that of a parallel plate capacitor. The capacity would then be

$$C_H = \frac{\epsilon_r \epsilon_0}{x_H} \dots\dots\dots (4)$$

where  $\epsilon_r$  is the relative permittivity (which is assumed not to vary with distance) and  $\epsilon_0$  the permittivity of vacuum  $x_H$  denotes the closest approach distance of point charges. The decay of the electrostatic potential from  $\phi_M$  to  $\phi_s$  is linear and  $C_H$  remains constant in the applied potential.

This model has two serious short comings:

1. The interactions with ions in the subsequent layers other than the first layer is neglected.

2. The dependence of electrolytic concentration on accumulation of charges in the double layer has not been taken into account. This model has been extended in the case of Gouy-Chapman Model (*Diffuse layer model*). In this model, It has been considered that the applied potential and electrolyte concentration both influenced the value of the double layer capacity. Thus, the double layer would not be compact as in Helmholtz's description but of variable thickness, since the ions being free to move (diffuse double layer) that there would be an equilibrium of the ions due to thermal and electrical fields in the double layer. The capacity of diffuse double layer is given as:

$$C_{d,GC} = \frac{\partial \sigma_M}{\partial \phi_{\Delta,0}} = \left( \frac{2x^2 e^2 \epsilon_r \epsilon_0 n_i^0}{k_B T} \right)^{1/2} \cosh\left(\frac{ze\phi_{\Delta,0}}{2k_B T}\right) \dots\dots (5)$$

The capacity varies with potential systematically with respect to point of zero charge  $E_z$ , which corresponds to the minimum in the curve. For dilute aqueous solutions at 298 K,

$$C_{d,GC} = 228zc_\infty^{1/2} \cosh(19.5z\phi_{\Delta,0}) \mu F \text{ cm}^{-2} \dots\dots(6)$$

This model is better than a parallel-plate capacitor but only close to  $E_z$ : in reality, far from  $E_z$ ,  $C_d$  is, to a first approximation, independent of potential. Combing these two models Stern considered that the double layer was formed by a compact layer of ions next to the electrode followed by a diffuse layer extending into the bulk solution. According to this theory, the total charge on the solution side is divided between the compact and diffuse layers, and is equivalent to two capacitors in series, with capacities,  $C_H$  representing the compact layer and  $G_{GC}$  representing the diffuse layer. The smaller of the two capacities determines the observed behavior:

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_{GC}} \dots\dots (7)$$

The total potential difference  $\phi$  between the metal and the bulk of the solution drops at first in a linear fashion  $\phi^M$  in the metal till it meets  $x_H$  and there after decays exponentially to  $\phi_S$  in the bulk of the solution.

There are two extreme cases for the variation of capacitance with potential:

- close to  $E_z$ ,  $C_H \gg C_{GC}$  and so  $C_d \sim C_{GC}$
- far from  $E_z$ ,  $C_H \ll C_{GC}$  and  $C_d \sim C_H$

For concentrated electrolyte solutions, the potential drop is rapid and hence the importance of the diffused double layer is reduced. At distance  $x_H$  there is a transition from the compact to the diffuse layer. The separation plane between the two zones is called the outer Helmholtz plane (OHP). Grahame developed a model that is constituted by three regions. The difference between this and the Stern model is the existence of specific adsorption: a specifically adsorbed ion loses its solvation, approaching closer to the electrode surface with strong bonding. The Inner Helmholtz plane (IHP) passes through the centers of these ions. The Outer Helmholtz plane (OHP) passes through the centers of the solvated and non-specifically adsorbed ions. The diffuse region is outside the OHP. In both the Stern and Grahame models, the potential varies linearly with distance until the OHP and then exponentially in the diffuse layer. Recent models of the double layer have taken into account the physical nature of the interfacial region. In dipolar solvents, such as water, it is clear that an interaction between the electrode and the dipoles must exist. This is reinforced by the fact that solvent concentration is always higher than solute concentration. For example, pure water has a concentration of  $55.5 \text{ mol dm}^{-3}$ . The model of Bockris, Devanathan, and Muller recognizes the solvation of the ions and shows the predominance of solvent molecules near the interface. The solvent dipoles are oriented according to the charge on the electrode where they form a layer together with the specifically adsorbed ions. Regarding the electrode as a giant ion, the solvent molecules form its first solvation layer; the IHP is the plane that passes through the centre of these dipoles and specifically adsorbed ions. In a similar fashion, OHP refers to adsorption of solvated ions that could be identified with a second solvation layer. Outside this comes the diffuse layer. These authors also defined a shear plane, not necessarily coincident with the outer Helmholtz plane, which is important in electro-

kinetic effects. The shear plane corresponds to the planes where the ions no longer influenced by the charge on the electrode. However, the concept of double layer structure is still evolving. The models developed so far emphasized electrostatic considerations. ‘Chemical’ models have been developed that consider the electronic distribution of the atoms in the electrode (especially solid electrodes, of different kinds which are related to their work functions. The variation of potential corresponding to the point of zero charge with the work function of the metal shows that sp metal follows a different linear relationship compared to transition metals. The models developed so far for the electrode/electrolyte interface have been successful to some extent and it is expected that appropriate models for describing the properties of the interface will evolve in the coming days.

## 2.5. Solid Metallic Electrode

Mercury is not a typical electrode material: it is liquid, and there is constant alleviation of atoms on the surface in contact with solution. A solid electrode has a well-defined structure (polycrystalline or monocrystalline). In solid metallic electrodes, the conduction is mainly due to the movement of free electrons at the Fermi surface, with energy  $E_F$  and following a Fermi-Dirac statistical distribution.

For a metal, the occupation of the electronic levels close to  $E_F$  is given by the expression:

$$f = 1/[1 + \exp (E - E_F)/k_B T] \quad \dots\dots (8)$$

where  $f$  is the probability of occupation of a level of energy  $E$  and  $k_B$  is the Boltzmann constant. The value of  $f$  is 0.50 when  $E = E_F$ . Fermi energy is therefore corresponds to the electrochemical potential of the electrons in the metal electrode. When  $E = E_F + k_B T$ ,  $f = 0.27$  and when  $E = E_F - k_B T$ ,  $f = 0.73$ . At  $T=0$ , the cut off of occupancy is sharp at  $E_F$ , while for higher temperatures ( $T>0$  K) the occupancy is smeared out. By convention, for a metal, electrons with energies within  $k_B T$  of  $E_F$  can only be transferred. The interfacial structure of a solid electrode depends on various factors like: (1) The inter atomic distances vary with the exposed crystallographic planes; (2) In a polycrystalline material one can have various kinds of defects; (3) Adsorption of species can be specific or non-specific.

The effects of the crystallographic face and the difference between different metals are evidence for the incorrectness of the classical representations of the interface with a universal type of potential decay within the solution. In fact a discontinuity at the interface is improbable and experimental evidences show that the electrostatic potential variation with distance may deviate from the value in the bulk electrode even certain distance from the interface inside the electrode. This corresponds to the 'chemical' models and reflects the fact that the electrons from the solid penetrate a tiny distance into the solution (due to wave properties of the electron). In this treatment the Galvanic (or inner electric) potential,  $\phi$ , (associated with  $E_F$ ) and the Volta (or outer electric) potential,  $\psi$ , that is the potential outside the electrode's electronic distribution (approximately at the IHP,  $10^{-5}$ cm from the surface) are distinguished from each other. The difference between these potentials is the surface potential.

## **2.6. Semiconductor Electrodes**

The essence of electrical conductivity is that charges must be able to move under an applied electrical field. In solids, conduction requires the movement of electrons. But for an electron to move there must be a partially vacant energy band. The electronic properties of solids are usually described in terms of the band model, in which the behavior of an electron moving in the field of the atomic nuclei and all of the other electrons is treated. The frontier electronic states in these solid materials are treated in terms of bands. These bands are separated by a forbidden region or band gap of energy  $E_g$ . When  $E_g \ll kT$  or when the conduction and valence bands overlap, the material is a good conductor of electricity.

In a semiconductor there is a separation between the occupied valence band and the unoccupied conduction band. By convention, if the separation is greater than 3eV the solid is called an insulator (for example diamond 5.4 eV) and if it is less it is a semiconductor. In a semiconductor electrode the accessible electronic levels are restricted, which has important consequences. Promotion of an electron from valence to conduction band leaves a hole (lack of electron), a positive charge. It is therefore essential to consider not only of electron movement but also of hole movement.

Conduction occurs by movement of electrons in the conduction band or of holes (lack of electrons) in the valence band.

In an intrinsic semiconductor electron promotion to the conduction band occurs through thermal or photo-excitation. Doping changes the distribution of electrons within the solid, and hence changes the Fermi level. For an n-type semiconductor, the Fermi level lies just below the conduction band, whereas for a p-type semiconductor it lies just above the valence band.

One needs to consider what happens at the (idealized) interface between a semiconductor electrode and an electrolyte solution. The anions that form the electrolyte region of the double-layer can approach the interface to the distance of the outer Helmholtz plane. Between this plane and the surface of the semiconductor there is a potential difference  $\phi_c$  so that the overall Galvani potential difference between the bulk of the semiconductor and the bulk of the electrolyte is given by the electrical potential differences in both diffuse double layers and  $\phi_c$ . At the surface of a semiconductor, surface energy levels may also form. An additional electrical potential difference due to the charge corresponding to these surface levels may contribute to the potential difference in the compact part of the double-layer.

The drop in the solution side is modified by a change in the composition of the solution, pH, and specifically adsorbed species and may not vary by the introduction of a redox couple which does not interact with the semiconductor. An equilibrium situation is attained with a potential drop,  $U_{SE}$ , in the space charge region below the semiconductor surface, leading to a certain bending of the energy bands. That is, in order for the two phases to be in equilibrium, their electrochemical potential must be the same. The electrochemical potential of the solution is determined by the redox potential of the electrolyte solution, and the redox potential of the semiconductor is determined by the Fermi level. If the redox potential of the solution and the Fermi level do not lie at the same energy, a movement of charge between the semiconductor and the solution is required in order to equilibrate the two phases. The excess charge that is now located on the semiconductor does not lie at the surface as it would for a metallic electrode, but

extends into the electrode for a significant distance (100-10,000 Å). This region is referred to as *space-charge region*, and has an associated electric field. Hence, there are two double layers to consider: the interfacial (electrode/electrolyte) double layer, and the space charge double layer.

For an n-type semiconductor electrode at open circuit, the Fermi level is typically higher than the redox potential of the electrolyte, and hence electron will be transferred from the electrode into the solution. Therefore, there is a positive charge associated with the space charge region, and this is reflected in an upward bending of the band edges. Since the majority charge carrier of the semiconductor has been removed from this region, this region is also referred to as a *depletion layer*. For a p-type semiconductor, the Fermi level is generally lower than the redox potential and hence electrons must transfer from the solution to the electrode to attain equilibrium. This generates a negative charge in the space charge region, which causes a downward bending in the band edges. Since the holes in the space charge region are removed by this process, this region again a depletion layer.

The band edges in the interior of the semiconductor (i.e., away from the depletion region) also vary with the applied potential in the same way as the Fermi level. However, the energies of the band edges at the interface are not affected by changes in the applied potential. Therefore, the change in the energies of the band edges on going from the interior of the semiconductor to the interface, and hence the magnitude and direction of band bending, varies with the applied potential. There are three different situations to be considered:

(1) At a certain potential, the Fermi energy lies at the same energy as the solution redox potential. There is no net transfer of charge, and hence there is no band bending. This potential is therefore referred to as the *flat band potential*,  $E_{fb}$ .

(2) Depletion region arise at potentials positive of the flat band potential for an n-type semiconductor and at potentials negative of the flat band potential for a p-type semiconductor.

(3) At potentials negative of the flat band potential for an n-type semiconductor, there is now an excess of the majority charge carrier (electrons) in this space charge region, which is referred to as an *accumulation* region. An accumulation region arises in a p-type semiconductor at potentials more positive than the flat band potential.

The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation layer or a depletion layer. If there is an accumulation layer, the behavior of a semiconductor electrode is similar to that of a metallic electrode, since there is an excess of the majority of charge carrier available for charge transfer, and electron transfer reactions occur slowly, if at all.

However, if the electrode is exposed to radiation of sufficient energy, electrons can now be promoted to the conduction band. If this process occurs in the interior of the semiconductor, recombination of the promoted electron and the resulting hole typically occurs, together with the production of heat. However, if it occurs in the space charge region, the electric field in this region will cause the separation of the charge. For example, for an n-type semiconductor at positive potentials, the band edges curve upwards and hence the hole moves towards the interface, and the electron moves to the interior of the semiconductor. The hole is a high energy species that can extract an electron from a solution species; that is the n-type semiconductor electrode acts as a photo-anode. At the flat band potential, there is no current, either in the dark or upon irradiation, since there is no electric field to separate any generated charge carriers. At potentials negative of the flat band potential, an accumulation layer exists, and the electrode can act as a cathode, both in the dark and upon irradiation (the electrode is referred to as a dark cathode under these conditions). At potentials positive of the flat band potential, a depletion layer exists, so there can be no oxidative current in the dark. However, upon irradiation, a photocurrent can be observed at potentials negative of the redox potential of the analyte (which lies at  $E^0$ ), since some of the energy required for the oxidation is provided by the radiation. Using similar reasoning, it can be taken that p-type semiconductor electrodes are dark anodes and photo-cathodes.

In a semiconductor electrode, almost all the potential variation in the interfacial region occurs in the space-charge region. This is because the values for the space-charge capacity,  $C_{sc}$ , are from  $0.001-1 \mu\text{F cm}^{-2}$ , whilst those for  $C_d$  are from  $10-100 \mu\text{F cm}^{-2}$ , so that  $C_{sc}$  dominates. The important situations one should stress are:

- For a certain value of applied potential, there is equality between the number of electrons removed from and supplied to the electrode. In this situation there will be no space-charge region and the potential is called the flat-band potential  $E_{fb}$ .
- Electrons accumulate in the space-charge layer by injection, giving rise to an accumulation layer.
- Electrons are removed from the space-charge layer, creating a depletion layer.

To have passage of current it is necessary that  $E_F$  is within the conduction or within the valence band in the space-charge region, i.e. accumulation layer in an n-type semiconductor (oxidation). For a p-type semiconductor the arguments are analogous; in this case the majority carrier is the hole.

The energy level of the lower edge of the conduction band of a semiconductor can be considered to be measure of the strength of the photo-excited electrons, whereas that of the upper edge of the valence band is a measure of the oxidation strength of the hole. Based on the potential of these semiconductors for oxidation and reduction reactions, the system can be classified into four groups.

(a) OR type: OR indicates a strong ability for both oxidation and reduction. The oxidation and reduction power is strong enough (in principle) for the evolution of both hydrogen and oxygen from water. Examples are  $\text{TiO}_2$ ,  $\text{SrTiO}_3$  and  $\text{CdS}$ .

(b) R type: Only the reduction power is strong enough to reduce water. The oxidation power is too weak to reduce water. Examples are  $\text{CdTe}$ ,  $\text{CdSe}$  and  $\text{Si}$ .

(c) O type: The oxidation power is strong enough to oxidize water since the valence band is located at a more positive value compared to the  $O_2/H_2O$  level. The reduction power is not strong enough to reduce water. Examples are  $WO_3$ ,  $Fe_2O_3$  and  $Bi_2O_3$ .

(d) X type: The conduction and valence bands are located between the  $H^+/H_2$  and  $O_2/H_2O$  levels. Therefore, both the oxidation and reduction powers are weak and neither oxygen nor hydrogen can be evolved. The use of semiconductors as electrode material has just started and interesting developments are expected in future.

## **2.7 Electro-kinetic phenomena and colloids:**

### **2.7.1. Zeta potential**

A colloidal system consists of a disperse phase suspended in a dispersion medium, which does not separate with time. All combinations of gases, liquids, and solids are possible except for a gas dispersed in a gas. Normally colloids refers to a solid suspended in a liquid, the solid particles having diameters between  $10^{-7}$  cm and  $10^{-5}$  cm. The solid particles are charged, which causes repulsion between the particles and offers temporal stability to the colloidal system. There has been increasing interest in colloids ( in addition to the nanotechnology) due to their possible use as electrodes for electrolysis, each particles acting as anode and cathode at a time. Their particular advantage is the large surface area exposed to solution in relation to their solid volume. Since the particles are charged there is an interfacial region, which exhibits many of the properties of the interfacial region of a solid electrode.

The electro-kinetic phenomenon that results from the movement of a solid phase with surface charge relative to an electrolyte-containing liquid phase is a useful phenomenon in case of colloidal particles. An applied electric field induces movement of ions or, movement of ions induces an electric field and this can be divided into two categories.

- Charged solid particles (colloidal particles) moving through the liquid under the influence of an electric field, *electrophoresis*, or due to gravitational force, *sedimentation*.

- Liquids moving past charged solid surfaces (or possibly through membranes) under the influence of an electric field, *electro-osmosis*, or an applied pressure difference, *streaming potential*. These effects are normally studied in fine capillaries in order to maximize the ratio of the solid surface area to the liquid volume.

The four manifestations of the electrokinetic effect are summarized in **Table 1**.

**Table 1.** Possible manifestations of Electro-kinetic phenomenon

<b>Mobile phase / Stationary phase</b>	<b>Phenomenon (Force applied)</b>	<b>Property measured</b>
Solid / Liquid	Electrophoresis (Electric field)	Electro-phoretic mobility via mass transport measurement, microscope or Doppler effect
Solid / Liquid	Sedimentation potential (Force of gravity)	Potential difference
Liquid / Solid	Electro-osmosis (Electric field)	Rate of liquid movement, pressure
Liquid / Solid	Streaming potential (Pressure)	Potential difference

The size of the particles that is calculated from these experiments corresponds to particle dimensions plus the double layer thickness. The shear plane is defined such that inside which the adsorbed species are rigidly held, and outside of which there is free movement. The shear plane can therefore be associated roughly with the outer Helmholtz plane. The value of the electrostatic potential at the shear plane with respect to the value in bulk solution is called the electro-kinetic or zeta potential,  $\xi$ .

In the presence of a large quantity of inert electrolyte, the entire potential drop is confined to within the compact layer and  $\xi$  is zero. By application of an appropriate potential at an electrode one can also achieve  $\xi = 0$ ; this value of the potential is called the iso-

electric point. This is, in fact, not equal to the point of zero charge, as the value of the latter is affected by the presence of specifically adsorbed species.

### ***2.7.2. Electrophoresis***

In electrophoresis the solid moves through a liquid phase due to the application of an electric field. The forces acting on the particles are similar to those that act on solvated ions:

- Force of the electric field on the particle
- Frictional forces
- Force due to the action of the electric field on ions of the opposite charge to that of the particle within the double layer (relaxation effect)
- Induction forces in the double layer caused by the electric field (electrophoretic retardation)

Normally, electro-phoretic mobility depends on ionic strength of the solution since double layer thickness decreases with increase in concentration of the electrolyte. It also depends on the surface charge of the particles. If this charge varies in colloidal particles of similar dimensions then electrophoresis provides a basis for their separation. For example, in proteins the surface charge varies with pH in a way according to the protein identity.

### ***2.7.3. Sedimentation Potential***

Colloidal particles are affected by the force of gravity, either natural or through centrifugation. Sedimentation of the particles often gives rise to an electric field. This occurs because the particles move, whilst leaving some of their ionic atmosphere behind. These potentials are usually difficult to measure and may cause undesirable side effect in ultracentrifugation. This can be minimized by the addition of large concentrations of inert electrolyte.

#### ***2.7.4. Electro-osmosis***

In electro-osmosis, the stationary and mobile phases are exchanged in relation to electrophoresis. Since the measurement of the rate of movement of a liquid through a capillary is difficult, the force that it exerts is measured, i.e. the *electro-osmotic pressure*, or, alternatively, the volume of liquid transported through a capillary in a given time interval.

#### ***2.7.5. Streaming potential***

If a pressure difference,  $\Delta P$ , is applied between the extremes of a capillary there exerts a potential difference, known as streaming potential. One can see a close relationship between streaming potential and electro-osmotic flow.

#### ***2.7.6. Limitations in the calculation of the zeta potential***

Quantitative measurements of electro-kinetic phenomena permit the calculation of the zeta potential by use of the appropriate equations. However, in the deduction of the equations certain approximations are made: this is because in the interfacial region physical properties such as concentration, viscosity, conductivity, and dielectric constant differ from the corresponding values in bulk solution, which is not taken into account. Corrections to compensate these approximations have been introduced, as well as consideration of non-spherical particles and particles of dimensions comparable to the diffuse layer thickness.

### **3. Prospects**

There are various factors to be considered from the basic electrochemistry point of view in designing suitable and viable fuel cells. However from a general point of view, the list of various factors that must be considered in devising electrochemical devices is given in Table 2. In this table the factors are given in the first column and the options and variables possible for experimentation are listed in the second column. Though most of the possible options are given in second column, it is possible other options also may be possible. The ones given are the most probable ones.

**Table 2.** The factors and options available for experimentation in electrochemical devices

Factors	Parameters or options for consideration
Goal	Analysis; Thermodynamics ; Kinetics; Mechanism Synthesis
Working electrode	Material of choice; Shape of the electrode; Size of the electrode; Rotation required or not? Pretreatment of the electrode- necessary or not
Ionic phase	Solvent; Analyte concentration; Product present or not Out-gassing is required or not
Other electrode	Spacing between electrodes; Reference or reaction; Junction potentials; Quasi reference
Supporting electrolyte	Is there a need for one? Should one use excess of this? Choice of supporting electrolyte; Has the supporting electrolyte be buffered?
Perturbation	Potential; Current; Single or both directions; Repetitive
Applied wave form	Step, ramp, pulse, square wave, ac or combination
Time resolution	Equilibrium; Steady state; Transient ;Frequency domain
Capacitive current	Should it be minimized? Should it be ignored ? Should it be blank subtracted
Ohmic polarization	Should it be ignored? Should it be compensated? Should it be measured and modeled.
Activation polarization	Is it reversible; Is it quasi-reversible; Is it irreversible
Concentration polarization	Diffusion controlling; Migration controlling Convection controlling
Chemistry	Homogeneous system ; Ion pairing occurs or not
Predictive modeling	Analytical model; Numerical model; Simulation model
Comparison of theory and experiment	Intuitively; Overlay; By data processing; Plot the data with normalization

The information given in Table 2 is more or less the summary of the electrochemical options one has for developing a viable fuel cell.

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