

APPLICATIONS OF ELECTROCHEMISTRY
IN MATERIALS SCIENCE & ENGINEERING
(MS 5180)

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1 INTRODUCTION

Any chemical reaction that involves a charge transfer, i.e. the transfer of electrons is an electrochemical reaction. In simpler terms, current + chemical reaction = electrochemical reaction. For an electrochemical reaction to occur, the following four components are essential:

- a) Anode: The electrode where oxidation occurs
- b) Cathode: The electrode where reduction occurs
- c) Electrolyte: A solid/liquid/molten salt solution essential for ionic transfer, and
- d) Conducting path: this could be a porous membrane or a salt bridge, depending on the type of cell.

An electrochemical cell/reaction is incomplete if any of the above components are missing. In order to have an electrochemical reaction, it is essential to have both the anodic and cathodic reactions simultaneously. Fig. 1 shows an illustration of a typical electrochemical cell.

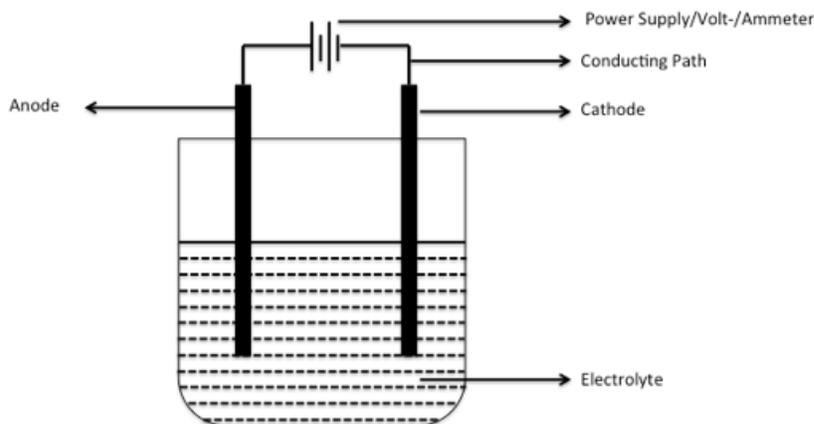


Figure 1: A SCHEMATIC ILLUSTRATION OF A TYPICAL ELECTRO-CHEMICAL CELL

1.1 TYPES OF ELECTROCHEMICAL CELLS

Depending on the nature of the electrochemical reaction, the electrochemical cells can be classified in to the following two categories (Fig. 2):

a) Galvanic cell: In this cell, when the anode and the cathode are brought together through a conducting path and an electrolyte, there is a spontaneous electrochemical reaction. The classical example is the Daniel Cell/Voltaic Cell involving Cu and Zn electrodes. Most commonly, the batteries we use in everyday applications fall in this category.

b) Electrowinning/Electrolytic cell: In this cell, after connecting the anode, cathode and electrolyte through a conducting path, an external power supply is required to carry out the electrochemical reaction. The reaction is non-spontaneous. Typical examples of such cells are electrolysis cells used for extracting pure metals, electrochemical cells used for thin film deposition.

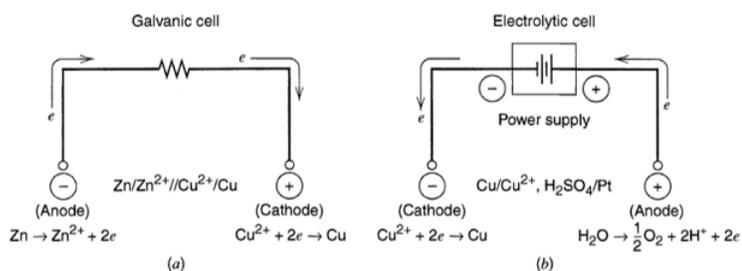


Figure 2: : EXAMPLES OF GALVANIC AND ELECTROLYTIC CELLS

1.2 PREREQUISITES FOR ELECTROCHEMICAL CELLS

As mentioned earlier, for an electrochemical reaction to occur, it is essential to have two half-cell reactions, i.e. the anodic (oxidation) reaction and the cathodic (reduction) reaction. These two half-cell reactions constitute the cell-reaction. Have a look at the example given below

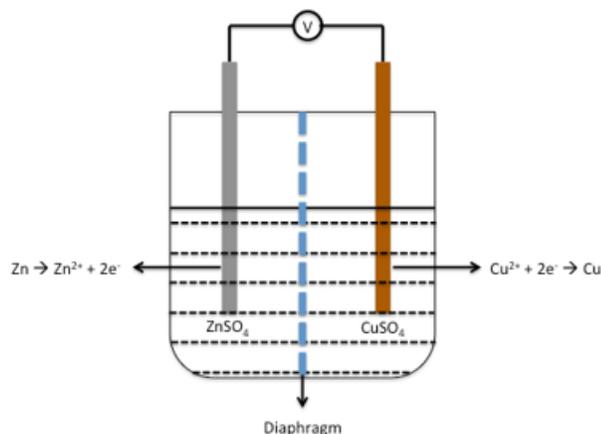
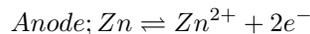
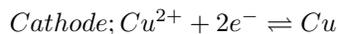


Figure 3: AN EXAMPLE OF GALVANIC CELL

The half cell reactions that constitute the cell reaction are:



(Oxidation reaction; dissolution, corrosion are examples of oxidation reactions)



(Reduction reaction; deposition is an example of reduction reaction)

The prerequisites for the half-cell reactions to occur are:

I. Need the presence of ions in the solution (electrolyte)

a. Dissolving a salt in an aqueous solution – examples are electrolysis of Cu, Zn, Ni etc.,

b. Molten salt electrolyte – Al electrolysis for example, the electrolyte is Al_2O_3 dissolved in $3NaF \cdot AlF_3$.

II. Mass transport of ions: Usually, the half-cell reaction occurs at the electrode-electrolyte interface, resulting in the consumption of ions or generation of excess ions at the interface in comparison with the bulk electrolyte. In order to sustain the half-cell reactions, mass transfer of the ions from bulk electrolyte to the

interface has to occur. In some cases, this is facilitated either by stirring the electrolyte or agitating the electrolyte by bubbling air.

III. Electroneutrality of the solution has to be maintained: The ions move from one half cell to the other, either through the porous membrane or through the salt bridge to maintain electroneutrality in bulk solution. Each of the half-cell electrolytes are termed as anolyte (anodic half-cell) and catholyte (cathodic half-cell). As the reaction progresses, the anolyte tends to get positively charged, whereas the catholyte tends to get negatively charged. In the example shown in Fig.3, the diffusion of SO_4^{2-} ions occurs through the porous membrane to maintain the electroneutrality.

IV. Flow of electrons: In a spontaneous electrochemical cell, a potential difference is created between the anode and the cathode.

Likewise in electrolytic/electrowinning cell, a potential difference has to be applied and as a result, there is a flow of electrons through the conducting path in between the electrodes.

2 HALF-CELL POTENTIALS, ORIGINS OF ELECTRODE POTENTIALS

2.1 THE ELECTRODE-ELECTROLYTE INTERFACE

As and when an electrode is introduced into an electrolyte, at the electrode-electrolyte interface spontaneous redox reactions start to occur. Consider the Zn half-cell from previous example shown in Fig. 3. If you zoom in to the electrode electrolyte interface (Zn-ZnSO₄ in this case a buildup of charge is observed as shown in Figure 4), see Fig. 4:

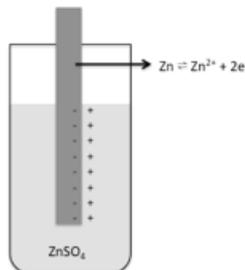
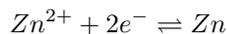


Figure 4: SCHEMATIC ILLUSTRATION OF THE ELECTRODE-ELECTROLYTE INTERFACE

To understand the potential associated with the half-cell reaction $Zn \rightleftharpoons Zn^{2+} + 2e^-$ we need to understand what is happening at the interface first. When Zn comes in contact with $ZnSO_4$ solution, at the interface Zn enters the solution as Zn^{2+} ions. Initially these Zn^{2+} ions cause a slight positive charge, i.e. a row of positively charged ions next to the interface. As a result of this row of positive charges, the forward reaction (see below), i.e. the Zn dissolution is slowed down.



Furthermore, there is a build up of the number of electrons that are left behind due to the formation of Zn^{2+} ions and this increases the rate of the following reaction:



This process of Zn dissolution and Zn deposition will continue till the rates of both the reactions are equal and a dynamic equilibrium is established. In an anode, the rate of dissolution is greater than rate of deposition initially and in case of a cathode the rate of deposition is higher than the rate of dissolution prior to dynamic equilibrium. Extending this to a general case, when a metal is immersed in an electrolyte, there is a build up of a double-layer of charges, called the electrical double layer and a dynamic equilibrium is established at the electrode-electrolyte interface. The double layer (DL) of charges acts as a barrier layer for either of the dissolution or deposition reactions to occur and this is the origin of half-cell electrode potentials.

2.2 MODELS OF ELECTRICAL DOUBLE LAYERS

Electrical double layer is one of the most fundamental concepts in electrochemistry; most of the electrochemical phenomena are attributed to various models of the double layer. The simplest model of the electrical double layer can be thought of as a simple parallel plate capacitor. Helmholtz first proposed this equivalent model. However, the parallel plate capacitor alone fails to explain most of the processes and hence more elaborate models have been developed and a few of them are briefly discussed here. These are: The Helmholtz, Gouy–Chapman, Stern, and Grahame models. Prior to introducing these models, it is important to understand the solvated nature of ions in aqueous solutions.

2.2.1 SOLVATED IONS

The charged ions in aqueous solutions themselves are surrounded by an outer sheath of water molecules, held by electrostatic forces to the ions themselves. The orientation of these water molecules differs when they surround cations or anions. This is due to the dipole nature of water molecules, as shown in Fig. 5. The same is also true for complex ions, which in comparison with simple ions have a more complex structure. The bonding between the central ion and the ligands is predominantly electrostatic or also non-polar bonding. The number of ligands is expressed as the so-called coordination number. There is no correlation between the valence number of the central ion and the coordination number, which is often 4, 6 or 8 in value.

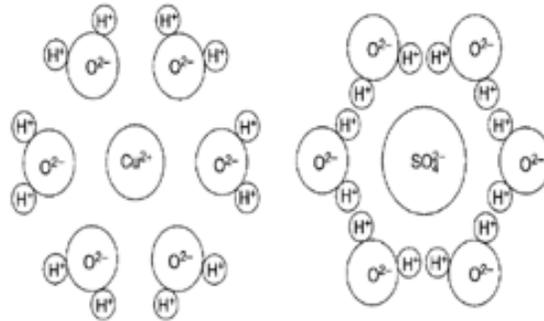


Figure 5: SOLVATED IONS IN A SOLUTION; NOTICE THE WATER SHEATH AND THE ORIENTATION OF DIPOLES AROUND THE CATION AND ANION RESPECTIVELY

2.2.2 HELMHOLTZ LAYER

Suppose an excess electric charge Q_m at the metal surface is in contact with a solution. This arrangement necessitates the formation of an equal and opposite charge Q_s at the solution side; Q_s is provided by ions present in the solution layer adjacent to metal surface. The simplest model (Fig. 6) of DL consists of two charges Q_m and Q_s distributed on two parallel planes, separated by a dielectric layer of solvent molecules (dipoles).

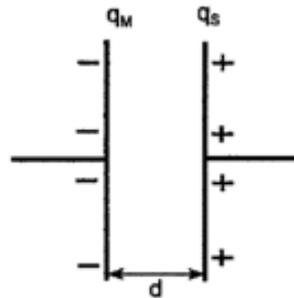


Figure 6: MODEL OF THE HELMHOLTZ DOUBLE LAYER, A SIMPLE PARALLEL PLATE CAPACITOR

In this model, the charges are assumed to be point-like and spaced by a distance x_o , determined by the size of the solvation sheath generated by the solvent

dipoles between the ionic layer and the metal surface. This region is of the order of 0.3 nm. The capacitance of such a capacitor is given by

$$C = \varepsilon_o \varepsilon_r A / d$$

where A is area and d is the distance between the two electrodes. ε_r is the relative permittivity in the region between the two charged layers. This space is filled by dipole molecules of the solvent but, due to the limited mobility of these dipoles, its permittivity is much less than that of the free solvent and assumed to be constant in $0 < x < d$. This model predicts a potential-independent capacitance, which is in contradiction with experiments that show capacitance dependence on potential. This suggests the interface, does not behave just as a simple capacitor and calls for more complex models.

2.2.3 DIFFUSE LAYER (GOUY-CHAPMAN LAYER)

In the Gouy-Chapman model, the ions are assumed as point charges and all the ionic interactions are assumed as purely electrostatic. According to this model, the ions from the surface of the electrode are distributed away from the surface into the solution, forming a diffuse layer of ions. It is theorized that these ions follow Maxwell-Boltzmann statistics. The diffuse layer consists of ions of both signs, with one sign being present in some excess, which gradually reduces with increasing distance from the electrode (Fig. 7). Gouy - Chapman model can be approximated for very dilute solutions and at potentials near the minimum. In concentrated solutions and at higher potentials, the theory is in disagreement with experimental results.

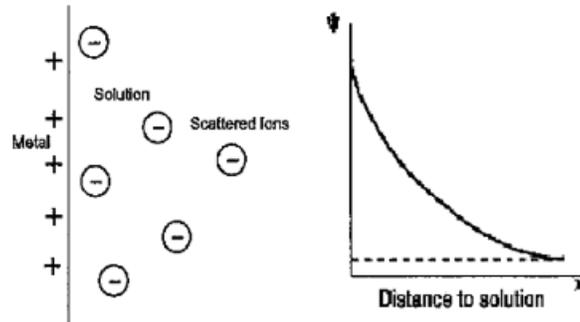


Figure 7: THE GOUY-CHAPMAN MODEL OF THE ELECTRICAL DOUBLE LAYER. THE IONS (BOTH POSITIVE AND NEGATIVE) FOLLOW MAXWELL-BOLTZMANN STATISTICS

2.2.4 STERN MODEL

The Stern model is a combination of the Helmholtz fixed (compact) layer and the Gouy–Chapman diffuse layer model (Fig. 8). According to the Stern model, some ions of excess charges are fixed, restricted to a single plane close to the metal, the Helmholtz excess charge q_H , and others are statistically distributed into the solution, the Gouy–Chapman excess charge q_{GC} . Thus, in this model the double layer is divided into two regions: the compact and the diffuse double layers: The compact double layer extends from the electrode to the plane of the fixed charges at a distance $x=x_H$ from the electrode. The diffuse double layer extends from the distance x_H to the bulk of the solution.

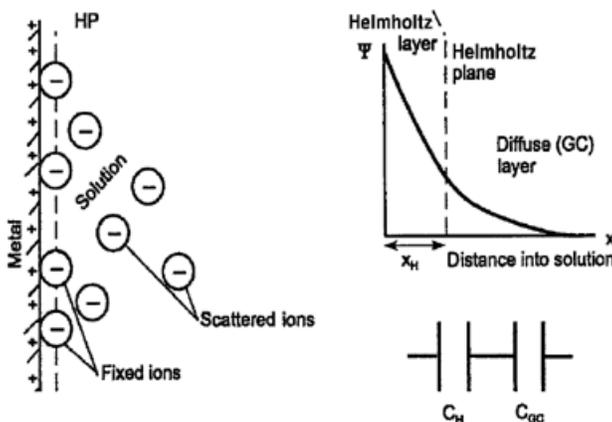


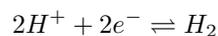
Figure 8: THE STERN MODEL OF THE ELECTRICAL DOUBLE LAYER. IN THIS MODEL THE ELECTRICAL EQUIVALENT OF THE DOUBLE LAYER CAN BE THOUGHT OF AS A COMBINATION OF TWO CAPACITORS IN SERIES

This is one of the most widely accepted models of double layer as it explains most of the electrochemical phenomena. However, it still has its own limitations. In the Gouy-Chapman and Stern models, distribution of the ions, the dependence of potential and its variation with distance is characterized by only one parameter, i.e. the valency of the ion, z . This means in all the electrolytes, all the equivalent ions behave in the same way. However, in practice, this is not always true. In order to overcome this drawback of the earlier models, there is also a triple-layer model proposed by Grahame, which is not discussed here.

2.3 ELECTRODE POTENTIALS, REFERENCE ELECTRODES & ELECTROCHEMICAL SERIES

In the discussion above, it is clear that there exists a double-layer across the electrode-electrolyte interface and the potential across the double layer is the origin of half-cell electrode potential. This potential can only be quantified when measured against standard reference electrodes.

Conventionally, the half-cell electrode potential for the hydrogen evolution reaction:



is considered as 0. This is interpreted as $E_{H^+/H_2}^o = 0$, at standard temperature and pressure (STP): i.e. the activity of ions is 1, Temperature is 298 K and the pressure of H_2 is 1 atm. Most of the half-cell electrode potentials are measured against the standard hydrogen reference electrode at STP, and there exists a series of electrochemical potentials, see Fig 9. For any given electrode, the potentials can be defined in terms of either oxidation reaction or the reduction reaction, however, the convention usually followed for half-cell potentials is in terms of standard reduction electrode potentials. The notation for standard reduction electrode potential a metal M is $E_{M^{n+}/M}^o$.

Elements	Electrode Reaction	E_{red}^o (volts)
<i>Oxidised Form + ne⁻ → Reduced Form</i>		
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
	$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	-0.41
Cd	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40
Pb	$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.31
Co	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
Sn	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.14
Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13
H₂	$2H^+ + 2e^- \longrightarrow H_2(g)$ (standard electrode)	0.00
Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
I ₂	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.54
Fe	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
Hg	$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.79
Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Hg	$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+0.85
N ₂	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.97
Br ₂	$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.08
O ₂	$O_2(g) + 2H_3O^+(aq) + 2e^- \longrightarrow 3H_2O$	+1.23
Cr	$Cr_2O_7^{2-} + 14H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
Cl ₂	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
Au	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.42
Mn	$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 12H_2O(l)$	+1.51
F ₂	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87

Figure 9: ELECTROCHEMICAL SERIES

As Standard Hydrogen Electrode (SHE) is not the most practical reference electrode for most of the electrochemical experiments, there also exist other standard reference electrodes such as the Saturated Calomel Electrode, Silver Reference Electrode etc., (Refer to your problem set for these details). Fig. 10a shows an example of Zn coupled with Ag electrode and Fig. 10b shows Ag electrode measured against SHE. This is an example where the reduction electrode potentials of Zn can be represented in terms of Ag reference electrode.

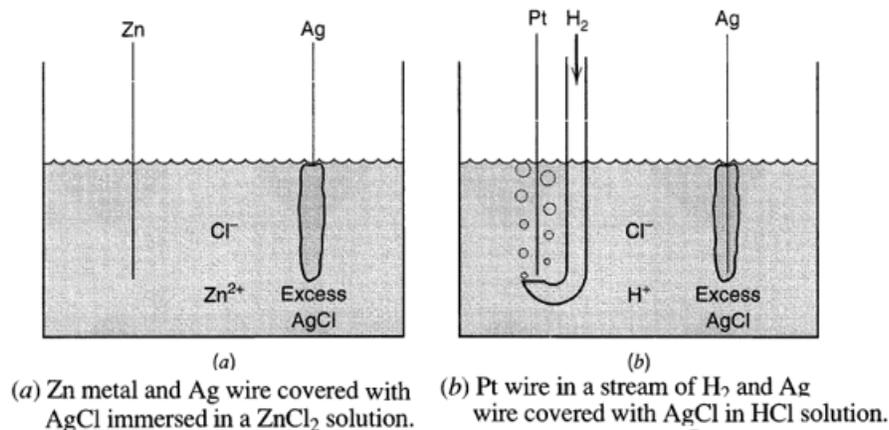
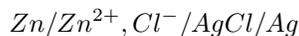


Figure 10: (A) ZINC MEASURED AGAINST SILVER REFERENCE ELECTRODE AND (B) SILVER-SILVER CHLORIDE REFERENCE ELECTRODE BEING MEASURED AGAINST STANDARD HYDROGEN REFERENCE ELECTRODE

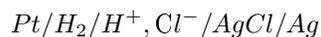
2.4 NOTATION FOR CELL POTENTIALS & ELECTRO-CHEMICAL CELLS

Before we consider how these operations are carried out, it is useful to set up a shorthand notation for expressing the structures of cells. For example, the cell pictured in Fig. 10a is written compactly as



In this notation, a slash represents a phase boundary, and a comma separates two components in the same phase. When a gaseous phase is involved, it is written adjacent to its corresponding conducting element. For example, the cell

in Fig. 10b is written schematically as



The phase of each chemical i.e. solid, liquid, gas and aqueous must be indicated as (s, l, g, aq.) in parentheses.

Consider the electrochemical cell shown in Fig. 11, where two half-cells of Cu in $Cu(NO_3)_2$ solution is connected to Ag in $AgNO_3$ solution through a salt bridge.

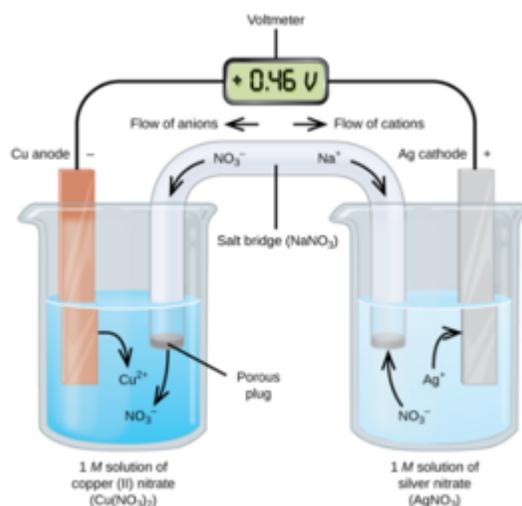
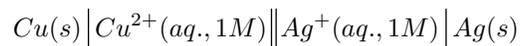


Figure 11: COPPER-SILVER ELECTROCHEMICAL CELL CONNECTED THROUGH A SALT-BRIDGE

The notation for the electrochemical cell in Fig. 11 is



A double slash used here, represents a phase boundary (in this case a salt bridge) whose potential is regarded as a negligible component of the overall cell potential.

2.5 NERNST EQUATION, THE TEMPERATURE DEPENDENCE OF ELECTRODE POTENTIALS

Half cell reactions usually correspond to standard conditions, that is (i) $a_{M^{n+}} = 1$, (ii) $T = 298 \text{ K}$, and (iii) for reactions involving gases, the partial pressure of the gas should be 1 atm. How do we determine the reduction potential, E , under non-standard conditions, that is when ionic activities or temperature or gas partial pressures are different from those under standard conditions? Here we use the Nernst equation.

The Nernst equation can be derived by considering a general cell reaction with reactants A, B, \dots and products M, N, \dots : and applying to this reaction the following below equations for the free-energy change, ΔG . Work done in bringing a charge q through a potential E is given by $W = qV$ but here $W = \Delta G$ and $q = nF$ (n is number of electrons involved and F is a Faraday Constant $\sim 96500 \text{ C}$).

For a reaction of the form $aA + bB + \dots = mM + nN + \dots$ we have,

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G = -nFE$$

We know that the standard gibbs free energy for a chemical reaction varies with temperature as,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\text{where } Q = \frac{\Pi[\text{Products}]}{\Pi[\text{Reactants}]}$$

$$-nFE = -nFE^\circ + \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\Pi[\text{Products}]}{\Pi[\text{Reactants}]}$$

According to Nernst's equation, there should be a linear relationship between the equilibrium potential of the metal/metal-ion electrode (M/M^{z+}) and the logarithm of the concentration of M^{z+} ions. This linear relationship was observed experimentally for a low concentration of the solute MA (e.g., 0.01 mol./L and lower). For higher concentrations, a deviation from linearity was observed. The deviation from linearity is due to ion-ion interactions. To account for this deviation Debye and Hückel developed the following equation to calculate the mean ionic activity coefficient γ . Here the activity coefficient γ (dimensionless quantity) depends on the concentration of all ions present in the solution (ionic strength I). where m_i is the concentration of species i in mol./L and z_i is the charge present on the ions. The constant ϵ is the dielectric constant of water whereas the T stands for temperature. The activity coefficient of individual ionic species cannot be measured experimentally but it can be calculated.

$$\log \gamma_{\pm} = \frac{-1.824 * 10^6}{(\epsilon T)^{1.5}} | Z_+ Z_- | I^{0.5}$$

$$\log \gamma_{\pm} = -0.509 | Z_+ Z_- | I^{0.5}$$

$$I = \frac{1}{2} \sum m_i z_i^2$$

2.6 FARADAYS LAWS OF ELECTROLYSIS

Faraday's First Law of Electrolysis states that , the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it. i.e. mass of chemical deposition.

Where, Z is a constant of proportionality and is known as electro-chemical equivalent of the substance. If we put $Q = 1$ coulombs , we will get $Z = m$ which implies that electro-chemical equivalent of any substance is the amount of the substance deposited on passing of 1 mole of electrons through its solution. This constant of passing of electro-chemical equivalent is generally expressed in terms of milligram per coulomb or kilogram per coulomb.

$$m = \frac{QM}{96485n}$$

It has been observed that the mass of the chemical, deposited due to electrolysis is proportional to the quantity of electricity that passes through the electrolyte. The mass of the chemical, deposited due to electrolysis is not only proportional to the quantity of electricity passes through the electrolyte, but it also depends upon some other factor. Every substance will have its own atomic weight. So for same number of atoms, different substances will have different masses. Again, how many atoms deposited on the electrodes also depends upon their number of valency. If valency is more, then for same amount of electricity, number of deposited atoms will be less whereas if valency is less, then for same quantity of electricity, more number of atoms to be deposited. So, for same quantity of electricity or charge passes through different electrolytes, the mass of deposited chemical is directly proportional to its atomic weight and inversely proportional to its valency.

Faraday's second law of electrolysis states that, when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

3 POLARIZATION

In most of the practical cases, for a galvanic cell, we observe that the cell potential, V_{cell} is always less than the theoretically predicted cell potential, E_{cell} . Likewise, for an electro-winning cell, the applied cell potential is always higher than the theoretically predicted value. This deviation in cell potential from the equilibrium value is termed as overpotential. The cause of this deviation is called polarization.

The question that arises is why is there a significant deviation from the theoretical value.

Consider the equilibrium situation; at equilibrium, there is no current flowing through the cell and both the half-cell reactions are at equilibrium. Now, when current starts flowing through the cell, several phenomena occur at both the electrodes. Firstly, the ions need to do work to go past the barrier of the electrical double layer. Secondly, the ions consumed (/generated) at the electrode-electrolyte interface need to be replenished by ions from the bulk electrolyte or transported to bulk solution to maintain electrical neutrality. And finally, as

the current flows through the cell, the resistance of the electrolyte, electrodes and other contact resistances cause an ohmic drop.

Deviation of potential from equilibrium potential because of net current flow is termed as polarization. Polarization is quantified by over potential (η).

ACTIVATION OVERPOTENTIAL (a) Energy involved in transporting M^{n+} across/towards the EDL.

The electrical energy associated due to the interaction between ion and Electric field of the double layer.

(b) Activation energy for the ($M^{n+} + ne \rightleftharpoons M$) reaction i.e either oxidation / reduction to happen. (Activation Energy of charge transfer reaction)

η_a^a : Activation overpotential at the anode.

η_c^c : Activation overpotential at the cathode.

CONCENTRATION OVERPOTENTIAL Concentration overpotential is used to defined the maximum permissible current flow in an electrolytic cell.

RSEISTANCE OVERPOTENTIAL Manifests as IR drop in the cell: predominant component of which is due to electrolyte resistance.

Note: Practically, the electrical equivalent of overpotential/polarization is a resistor.

$$V_{cell} = E_{cell} \pm [(|\eta_a^c| + |\eta_a^a| + |\eta_c^a| + |\eta_c^c|) + jRA]$$

$$V_{cell}(spontaneous) < E_{cell} < V_{cell}(non - spontaneous)$$

4 ARRHENIUS EQUATION & POTENTIAL ENERGY SURFACES

Most rate constants of solution-phase reaction vary with temperature in a common way: $\ln k$ is linear with $1/T$. Arrhenius was the first to recognize the

generality of this behavior, and proposed the below expression for rate constants.

$$k = Ae^{-E_A/RT} \quad (1)$$

E_A : Activation Energy

T : Temperature

k : Rate Constant

If the exponential term expresses probability of crossing the energy barrier, then A must be related to the frequency of attempts and is generally known as frequency factor. The idea of activation energy has led to pictures of reaction path in terms of potential energy along a reaction coordinate. So, the reaction coordinate expresses progress along a favored path on the multidimensional surface describing potential energy as a function of all independent position coordinates in the system. One zone of this surface corresponds to the configuration we call “reactant” and the other corresponds to the structure of the “product”. Both must occupy minima on the surface, because they are the only arrangements possessing a significant lifetime. Even though other configurations are possible, they must lie at higher energies and lack the energy minima required for stability.

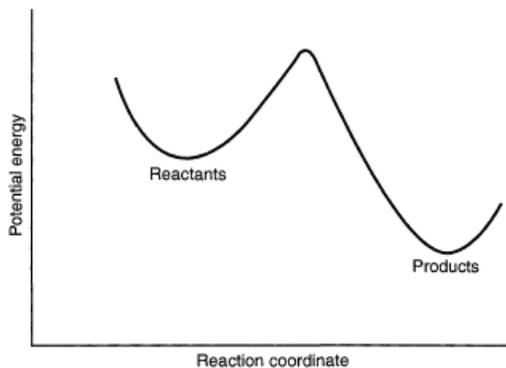


Figure 12: SIMPLE REPRESENTATION OF POTENTIAL ENERGY CHANGES DURING A REACTION

We can understand E_A as the change in standard internal energy in going from one of the minima to the maxima, which is called the transition state or the

activated complex. We must designate it as the standard internal energy of activation, ΔE .

The standard enthalpy of activation, ΔH , would be $\Delta E + \Delta(PV)$, but $\Delta(PV)$ is usually negligible in a condensed phase reaction, so that $\Delta H \approx \Delta E$.

$$k = Ae^{-\Delta H/RT} \quad (2)$$

Standard entropy of activation is given by ΔS . We are free to factor the coefficient A into the product $A'e^{\Delta S/R}$ because the exponent involving the standard entropy of activation ΔS , is a dimensionless constant.

$$k = Ae^{-(\Delta H - T\Delta S)/RT} \quad (3)$$

$$k = A'e^{-\Delta G/RT} \quad (4)$$

ΔG : Standard free energy of activation.

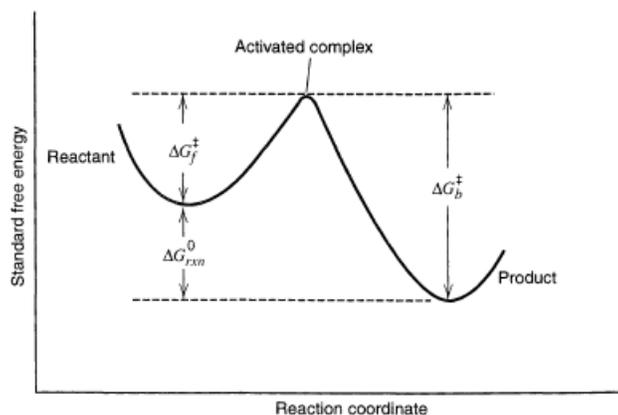


Figure 13: ACTIVATION COMPLEX/TRANSITION STATE

The forward reaction proceeds at a rate, v_f , that must be proportional to the surface concentration of O. The concentration at a distance x from the surface and at a time t is $C_o(0, t)$. The constant of proportionality linking the forward reaction rate to $C_o(0, t)$ is the rate constant k_f .

$$v_f = k_f C_o(0, t) = \frac{i_c}{nFA} \quad (5)$$

Note 1: i (amperes) = $\frac{dQ}{dt}$ (coloumb/s)

$$\frac{Q(\text{coloumb})}{nF(\text{coloumb/mol})} = N \text{ (mol electrolyzed)}$$

where n , is the stoichiometric number of electrons consumed in the electrode reaction.

$$\text{Rate}(\text{mol/s}) = \frac{dN}{dt} = \frac{i}{nF}$$

Interpreting the rate of an electrode reaction is often more complex than doing the same for a reaction occurring in the solution or in the gas phase. The latter is called a homogeneous reaction, because it occurs everywhere within the medium at a uniform rate. In contrast, an electrode process is a heterogenous reaction occurring only at the electrode - electrolyte interface. Its rate depends on mass transfer to the electrode and various surface effects, in addition to the usual kinetic variables.

Since electrode reactions are heterogenous, their reaction rates are usually described in units of $\frac{\text{mol}}{\text{s.cm}^2}$.

$$\text{Rate}(\text{mol/s.cm}^2) = \frac{i}{nAF} = \frac{j}{nF}$$

Note 2 : Current density dictates the kinetics of the reaction.

Since the forward reaction is a reduction reaction, there is a cathodic current, i_c , proportional to v_f .

Likewise, we have for the backward reaction.

$$v_b = k_b C_R(0, t) = \frac{i_a}{nFA} \quad (6)$$

where i_a is the anodic component of the total current. Thus the net reaction rate and net current are described as

$$v_{net} = v_f - v_b = k_f C_o(0, t) - k_b C_R(0, t) = \frac{i}{nFA} \quad (7)$$

$$i = i_c - i_a = nFA[(k_f C_o(0, t) - k_b C_R(0, t))] \quad (8)$$

Note that heterogenous reactions are described differently as mentioned previously. For example, reaction velocities in these systems have units $\frac{mol}{s.cm^2}$. Thus heterogenous rate constants must carry units of $\frac{cm}{s}$, if the concentrations on which they operate are expressed in $\frac{mol}{cm^3}$.

Note: Since the interface can respond only to its immediate surroundings, the concentrations entering rate expressions are always surface concentrations, which may differ from those of the bulk solution.

5 BUTLER VOLMER MODEL OF ELECTRODE KINETICS

Consider the simplest possible electrode process, wherein species O and R engage in a one-electron transfer $O + e \rightleftharpoons R$ at the interface without being involved in any other chemical step. Suppose also that the standard free energy profiles along the reaction coordinate have the parabolic shapes shown in Figure 3. The upper frame of that figure depicts the full path from reactants to products, while the lower frame is an enlargement of the region near the transition state. Suppose the upper curve on the $O + e$ side of Figure 3 applies when the electrode potential is equal to $E^{o'}$. The cathodic and anodic activation energies are then ΔG_{oc} and ΔG_{oa} respectively. If the potential is changed by ΔE to a new value, E, the relative energy of the electron resident on the electrode changes by $-F\Delta E = -F(E - E^{o'})$; hence the $O + e$ curve moves up or down by that amount. The lower curve on the left side of Figure 3 shows this effect for a positive ΔE . It is readily apparent that the barrier for oxidation, ΔG_a , has become less than ΔG_{oa} by a fraction of the total energy change. Let us call that fraction $(1 - \alpha)$ where α , the transfer coefficient, can range from zero to unity, depending on the shape of the intersection region. Thus,

$$\Delta G_a = \Delta G_{oa} - (1 - \alpha)F(E - E^{o'}) \quad (9)$$

A brief study of the figure also reveals that at potential E the cathodic barrier, ΔG_c , is higher than ΔG_{oc} by $\alpha F(E - E^{o'})$; therefore,

$$\Delta G_c = \Delta G_{oc} + \alpha F(E - E^{o'}) \quad (10)$$

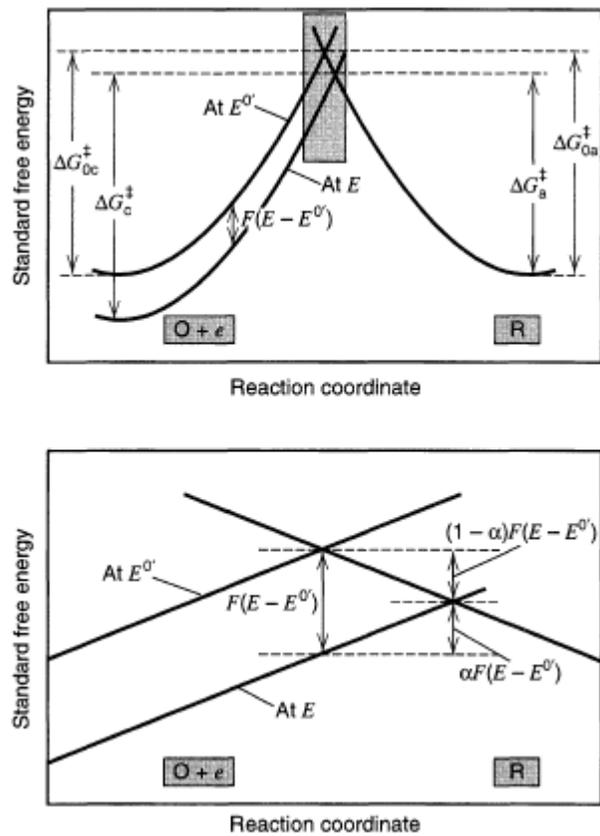


Figure 14: EFFECTS OF A POTENTIAL CHANGE ON THE STANDARD FREE ENERGIES OF ACTIVATION FOR OXIDATION AND REDUCTION. THE LOWER FRAME IS A MAGNIFIED PICTURE OF THE BOXED AREA IN THE UPPER FRAME

Now let us assume that the rate constants k_f and k_b have an Arrhenius form that can be expressed as following;

$$k_f = A_f e^{(-\Delta G_c/RT)} \quad (11)$$

$$k_b = A_b e^{(-\Delta G_a/RT)} \quad (12)$$

Plugging in the activation energies gives,

$$k_f = A_f e^{(-\Delta G_{oc}/RT)} . e^{-\alpha f(E-E^{o'})} \quad (13)$$

$$k_b = A_b e^{(-\Delta G_{oa}/RT)} . e^{(1-\alpha)f(E-E^{o'})} \quad (14)$$

where $f = \frac{F}{RT}$. The first two factors in each of these expressions form a product that is independent of potential and equal to the rate constant at $E = E^{o'}$.

Now consider the special case in which the interface is at equilibrium with a solution in which $C_O^* = C_R^*$. In this situation, $E = E^{o'}$ and $k_f.C_O^* = k_b.C_R^*$, so that $k_f = k_b$. Thus, $E^{o'}$ is the potential where the forward and reverse rate constants have the same value. That value is called the standard rate constant, k^o . The rate constants at other potentials can then be expressed simply in terms of k^o .

$$k_f = k^o e^{-\alpha f(E-E^{o'})} \quad (15)$$

$$k_b = k^o e^{(1-\alpha)f(E-E^{o'})} \quad (16)$$

Substituting these into Eq [8] we get the following expression for current;

$$i = F A k^o \left[e^{-\alpha f(E-E^{o'})} C_O(0, t) - k^o e^{(1-\alpha)f(E-E^{o'})} C_R(0, t) \right] \quad (17)$$

5.1 EQUILIBRIUM CONDITIONS: THE EXCHANGE CURRENT

At equilibrium, the net current is zero, and the electrode is known to adopt a potential based on the bulk concentrations of O and R as dictated by the Nernst equation.

$$FAk^o e^{-\alpha f(E_{eq}-E^{o'})} C_O(0, t) = FAk^o e^{(1-\alpha)f(E-E^{o'})} C_R(0, t) \quad (18)$$

Since equilibrium applies, the bulk concentrations of O and R are found also at the surface; hence

$$e^{f(E_{eq}-E^{o'})} = \frac{C_O^*}{C_R^*} \quad (19)$$

which is simply an exponential form of the Nernst relation;

$$E_{eq} = E^{o'} - \frac{RT}{F} \ln \frac{C_R^*}{C_O^*} \quad (20)$$

Even though the net current is zero at equilibrium, we still envision balanced faradaic activity that can be expressed in terms of the exchange current, i_o , which is equal in magnitude to either component current, i_c or i_a . i.e;

$$i_o = FAk^o C_O^* e^{-\alpha f(E_{eq}-E^{o'})} \quad (21)$$

5.2 CURRENT OVERPOTENTIAL EQUATION

Raising both sides of Equation [19] by $-\alpha$, we get

$$e^{-\alpha f(E_{eq}-E^{o'})} = \left(\frac{C_O^*}{C_R^*} \right)^{-\alpha} \quad (22)$$

Substituting into Equation [21] yields,

$$i_o = FAk^o C_O^{*(1-\alpha)} \cdot C_R^{*\alpha} \quad (23)$$

The exchange current is therefore proportional to k^o and can often be substituted for k^o in kinetic equations. For the particular case where $C_o^* = C_R^* = C$,

$$i_o = F A k^o C \quad (24)$$

$$j_o = F k^o C \quad (25)$$

An advantage of working with i_o rather than k^o is that the current can be described in terms of the deviation from the equilibrium potential, that is, the overpotential, η , rather than the formal potential, E^o . Dividing Equation [17] by Equation [23] we get,

$$\frac{i}{i_o} = \left[\frac{e^{-\alpha f(E-E^o)} C_O(0,t)}{C_O^{*(1-\alpha)} C_R^{*\alpha}} - \frac{e^{(1-\alpha)f(E-E^o)} C_R(0,t)}{C_O^{*(1-\alpha)} C_R^{*\alpha}} \right] \quad (26)$$

$$\frac{i}{i_o} = \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f(E-E^o)} \left(\frac{C_O^*}{C_R^*} \right)^\alpha - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha)f(E-E^o)} \left(\frac{C_O^*}{C_R^*} \right)^{-(1-\alpha)} \right] \quad (27)$$

The ratios $\left(\frac{C_O^*}{C_R^*} \right)^\alpha$ and $\left(\frac{C_O^*}{C_R^*} \right)^{-(1-\alpha)}$ can be evaluated from Equations [19] & [22] and upon substitution into Equation [27] we get the final expression of the form

$$i = i_o \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha)f \eta} \right] \quad (28)$$

where $\eta = E - E_{eq}$. This equation is known as the current overpotential equation.

5.3 APPROXIMATE FORMS OF THE CURRENT OVERPOTENTIAL EQUATION

NO MASS TRANSFER EFFECTS:

If the solution is well stirred, or currents are kept so low that the surface concentrations do not differ appreciably from the bulk values, equation [28] can be written as shown in equation [29], which is historically known as Butler-Volmer equation.

$$i = i_o \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right] \quad (29)$$

Butler volmer equation in terms of activation overpotential and in terms of current density is described by the below equations.

$$j_a = j_o e^{\frac{(1-\alpha)nF\eta_a}{RT}} \quad (30)$$

$$\log j_a = \log j_o + \frac{2.303(1-\alpha)nF\eta_a}{RT} \quad (31)$$

$$j_c = j_o e^{\frac{-\alpha nF\eta_a}{RT}} \quad (32)$$

$$\log j_c = \log j_o - \frac{2.303\alpha nF\eta_a}{RT} \quad (33)$$

5.4 TAFEL BEHAVIOUR

For large values of η_a (either negative or positive), one of the terms in the equation 29 becomes negligible. For example, at large negative overpotentials, $\exp(-\alpha f \eta) \gg \exp[(1-\alpha) f \eta]$ and equation [29] is reduced to the below

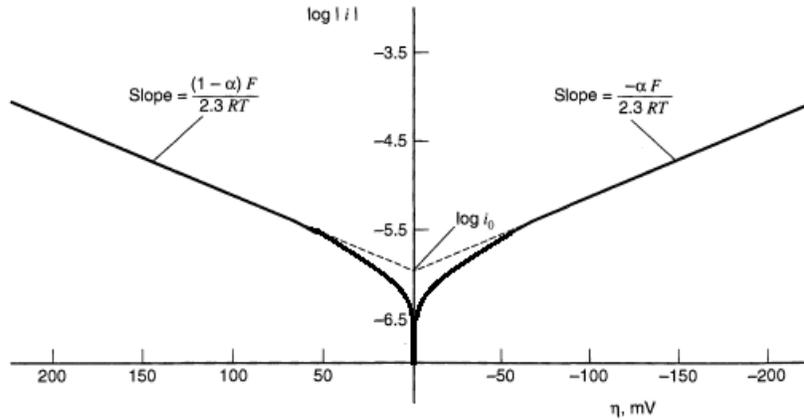


Figure 15: TAFEL PLOTS FOR ANODIC AND CATHODIC BRANCHES OF THE CURRENT-OVERPOTENTIAL CURVE FOR $O + e^* \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K

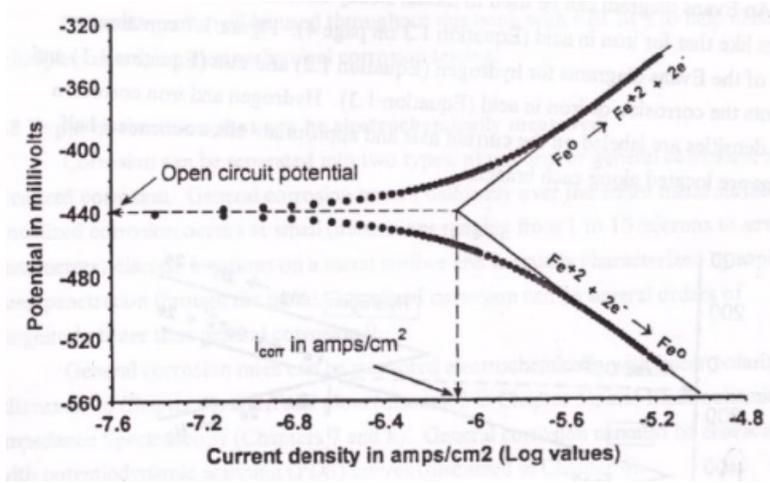


Figure 16: THEORETICAL (STRAIGHT LINES) AND EXPERIMENTAL CURVES (DOTTED LINES) FOR REDOX REACTION $\text{Fe}^{2+} + 2\text{e}^-$ IN TAFEL REGIME

$$j = j_o e^{-\alpha f \eta} \quad (34)$$

$$\eta_a = \frac{RT}{\alpha F} \ln j_o - \frac{RT}{\alpha F} \ln j \quad (35)$$

6 MASS TRANSPORT IN ELECTROCHEMICAL CELLS

There are three main mechanisms involved in delivery of ions (Mass Transfer) to the electrode surface, these being Migration: Voltage applied across the electrodes of an electrolysis cell sets up an electrical field between anode and cathode. The magnitude of this potential gradient determines the rate at which ions move through solution. The effect operates throughout the solution, anions being electrostatically attracted to the anode, cations to the cathode. The progress of such ions through solution is impeded by collisions with solvent molecules and viscous drag as the ions, with their hydration sheaths, move through the liquid. The ions thereby acquire a given velocity, depending on the

nature of the ion, the potential gradient, solution viscosity, etc. These velocities are very low, of the order of micrometers per second. It follows that the overall contribution to the supply of ions resulting from the migration process is very small, and can generally be neglected. Convection: Can be said to be the movement of reactants, etc. within the electrolyte. This so-called 'convective mass transport' results from movement of the bulk solution, whether by stirring (forced convection) or by the natural circulation (density differences caused by thermal effects). Diffusion: The penultimate step, before charge transfer takes place at the electrode surface, is the migration of species, both charged and uncharged, across the diffuse layer. The driving force here is the concentration gradient, more formally expressed as chemical potential. The tendency of species to move from regions of high concentration to those of lower concentration, are what drive the diffusion process, and this is enshrined in Fick's laws of diffusion. Without forced convection, in a static solution, the diffuse layer would be approx. 0.2 mm. and under forced convection, this value can reach values as low as 0.001 mm. The Nernst–Planck equation below relates the unidirectional (x) flux of a species j to diffusion, migration, and convection

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \mu_{m^{n+}} C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad (36)$$

where $J_i(x)$ [mol.cm⁻².s⁻¹] is a one-dimensional flux for species j at distance x [cm] from the electrode; D_i [cm².s⁻¹], $\mu_{m^{n+}}$ is the concentration gradient and C_i [mol.cm⁻³] are the diffusion coefficient, the charge, and the concentration for the species j, respectively; $v(x)$ [cm.s⁻¹] is the rate with which a volume element moves in solution; $\frac{\partial C_i(x)}{\partial x}$ is the concentration gradient; and $\frac{\partial \phi(x)}{\partial x}$ is the potential gradient along the x-axis. In the above equation, the first term is concerned with the diffusion and is, in fact, Fick's first law, the second term accounts for the migration of the species in the solution, and the last term represents the convection of the solution.

6.1 EFFECT OF CONCENTRATION OVERPOTENTIAL ON CURRENT DENSITY

The previous sections have given an elaborate insight on activation overpotential, which is primarily due to the migration of ions. The major contribution for concentration overpotential is from the diffusion component of mass transport

in electrochemical cells. The flux for diffusion is usually described by Fick's law as stated above, which relates the diffusive flux to the concentration under the assumption of steady state. Flux due to diffusion is given by the Fick's first law of diffusion. Now let us look at the electrode electrolyte interface closely (see Fig 17).

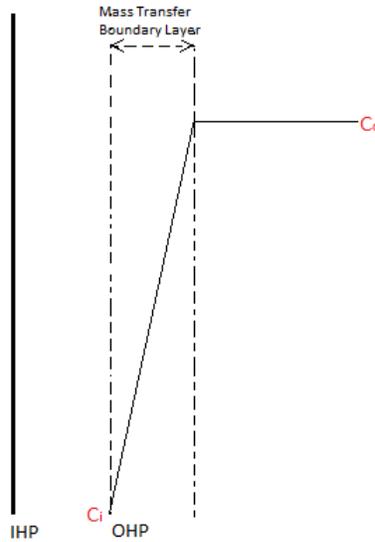


Figure 17: CONCENTRATION GRADIENT BETWEEN BULK AND INTER-FACE

Here, as the ions are consumed at the electrode, there is a drop in concentration at the interface. Along the x-axis (unidimensional diffusion in this case) the distance after which the gradient in the concentration stops and reaches bulk concentration is termed as the mass transport boundary layer (δ).

From Fick's first law of diffusion,

$$J_i = -D_i \frac{dC_i}{dx} \quad (37)$$

In this case, from Faraday's laws of electrolysis, we know the flux at the electrode is $\frac{j}{nF}$. (Refer section 4 for this derivation)

Equating the flux due to diffusion from Fick's law,

$$\frac{j}{nF} = \frac{-D(C_o - C_i)}{\delta} \quad (38)$$

As you can see, the flux due to diffusion reaches a maximum value when the interfacial concentration, $C_i = 0$.

$$j_{max} = \frac{-D_i C_o}{\delta} \quad (39)$$

In order to relate the concentration overpotential to the current density, we know from the Nernst equation we know that V_{cell} is (note that the concentration is C_i here) and ($\eta_c^c \neq 0$)

$$V_{cell} = E_{M^{n+}/M}^o - \frac{2.303}{RT} \log \frac{a_m}{C_i} \quad (40)$$

If there was no concentration overpotential ($\eta_c^c = 0$),

$$E_{cell} = E_{M^{n+}/M}^o - \frac{2.303}{RT} \log \frac{a_m}{C_o} \quad (41)$$

In order to estimate the concentration overpotential,

$$\eta_c^c = V - E \quad (42)$$

Concentration overpotential can now be written as,

$$\eta_c^c = V - E = \left[\frac{-2.303RT}{nF} \log \left(\frac{1}{C_i} \right) + \frac{2.303RT}{nF} \log \left(\frac{1}{C_o} \right) \right] \quad (43)$$

$$\eta_c^c = \frac{2.303RT}{nF} \log \left(\frac{C_i}{C_o} \right) \quad (44)$$

Anodic Reaction:

$$V = E_{M/M^{n+}}^o - \frac{2.303}{RT} \log C_i \quad (45)$$

$$E = E_{M/M^{n+}}^o - \frac{2.303}{RT} \log C_o \quad (46)$$

$$\eta_c^a = V - E = \left[\frac{-2.303RT}{nF} \log C_i + \frac{2.303RT}{nF} \log C_o \right] \quad (47)$$

$$\eta_c^a = \frac{2.303RT}{nF} \log \left(\frac{C_o}{C_i} \right); \frac{C_o}{C_i} > 1 \quad (48)$$

6.2 LIMITING CURRENT DENSITY

As described in above section, the flux due to diffusion reaches a maximum value when the concentration at the interface C_i is 0. The current density associated with this is limiting current density. This is the maximum value of current density due to diffusion.

$$\frac{j_L}{nF} = \frac{-D_{M^{n+}} C_o}{\delta} \quad (49)$$

$$\frac{j_c}{nF} = \frac{-D_{M^{n+}} (C_o - C_i)}{\delta} \quad (50)$$

$$\frac{j_c}{j_L} = 1 - \left(\frac{C_i}{C_o} \right) \quad (51)$$

$$\frac{C_i}{C_o} = 1 - \frac{j_c}{j_L} \quad (52)$$

$$\eta_c^c = \frac{2.303RT}{nF} \log \left(1 - \frac{j_c}{j_L} \right) \quad (53)$$

Note: Following a similar procedure will give the concentration overpotential for the anodic side.

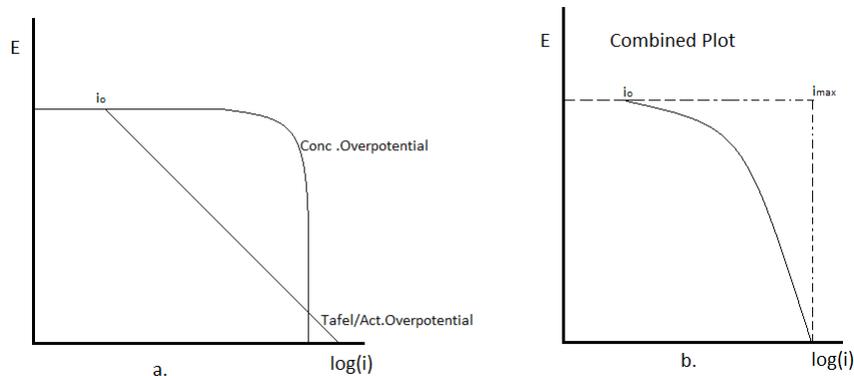


Figure 18: (A) E vs log i FOR CONCENTRATION OVERPOTENTIAL AND ACTIVATION POTENTIAL (B) COMBINED PLOT SHOWING THE INFLUENCE OF BOTH CONCENTRATION AND ACTIVATION OVERPOTENTIAL

Fig 18 (A) shows the behaviour of current for activation and concentration overpotentials individually. From the Butler-Volmer equation we get the Tafel approximation, where we only consider the activation overpotential. The Tafel equation is based on a logarithmic relation and hence we get a straight line as shown in the figure above.

Whereas for concentration overpotential we have an asymptotic curve. When an experiment is performed we have both the activation and concentration overpotentials and as a result we get a curve as shown in Fig 18(B), which is seen to reach the limiting current density value i_{max} .

7 REVISITING POLARIZATION

Let us revisit the polarization again to understand its mathematical form. These equations are useful in understanding experimental results obtained through electrochemical methods.

ACTIVATION POLARIZATION There is an activation barrier that exists at the metal-electrolyte interface (Electrical Double Layer) and it is through this activation barrier that the metal atoms have to pass into solution as ions or

the ions from the solution pass (plated on) the surface. The impetus for these processes is provided by electron removal from the material or electron flow into the material, respectively, which is termed as the activation overvoltage. Anodic and cathodic activation overpotentials are given by the following equations:

$$\eta_a^a = \beta_a \log \left(\frac{i_a}{i_o} \right) \quad (54)$$

$$\eta_a^c = \beta_c \log \left(\frac{i_c}{i_o} \right) \quad (55)$$

$$\text{where, } \beta_a = \frac{2.303RT}{\alpha nF}; \beta_c = \frac{2.303RT}{(1 - \alpha)nF}$$

These equations are simplified versions of the Butler-Volmer Equation for low values of overpotential ($\pm 100\text{mV}$), known as the Tafel equations, where η_a^a and η_a^c are anodic and cathodic activation polarizations, β_a and β_c are the Tafel constants, i_a and i_c are the anodic and cathodic current densities, and i_o is the exchange current density.

CONCENTRATION OVERPOTENTIAL It refers to the condition in which actual departure of reversible potential is caused by concentration gradient of metallic ions between electrode-electrolyte interface and the bulk electrolyte.

$$\eta_c^c = \frac{2.303RT}{nF} \log \left\{ 1 - \frac{i}{i_{max}} \right\} \quad (56)$$

Where n is the number of electron transfer taking place in the reaction, and i_{max} stands for maximum reaction rate that cannot be exceeded because of limited ionic diffusion. Combining the above two types of polarizations effect for deposition, equation for total polarization is:

$$\eta = \eta_{activation} + \eta_{concentration}$$

$$\eta = \beta_c \log \left(\frac{i_c}{i_o} \right) + \frac{2.303RT}{nF} \log \left\{ 1 - \frac{i}{i_{max}} \right\} \quad (57)$$

RESISTANCE POLARIZATION There is generally a finite potential drop in the solution between the reference electrode that is measuring the potential and the actual metal surface. This is termed as resistance polarization and mathematically can be defined as,

$$\eta_{resistance} = ri$$

Where 'r' is the resistance for 1 cm² of area (in units of ohm/cm²) and 'i' is the current density in amp/cm².

8 EXPERIMENTAL TECHNIQUES IN ELECTROCHEMISTRY

For most of the electrochemical experiments, we use a 3-electrode system. These are (i) Working Electrode (WE) – the reaction of interest occurs here (could be cathodic/anodic) (ii) Counter (auxiliary) Electrode (CE/AE)– the supporting reaction occurs here (iii) Reference Electrode (RE) – the potential across the electrical double layer of the working-electrode – electrolyte interface is monitored through out the experiment.

What do we do in the electrochemical experiments? (i) Monitor voltage drop across the EDL of the WE (ii) Monitor the variations in the cell current

Typically the area of the Counter Electrode is significantly more than the Working Electrode. Since we are interested in the overpotential characteristics of the reactions occurring at the working electrode only, we would like to ensure that the overpotential for the counter electrode is close to zero (approximately zero or negligible. This is achieved in two ways:

(i) Increase the area of counter electrode significantly more than the working electrode, such that the current density at CE is much less than current density at WE.

(ii) Use an ideally non-polarizable electrode (Pt): it is a type of electrode that does not change its potential upon passage of current; example: reference electrode.

Potentiostat: A potentiostat can be thought of as a highly sensitive voltmeter and ammeter with a very high resistance such that minute voltages and currents

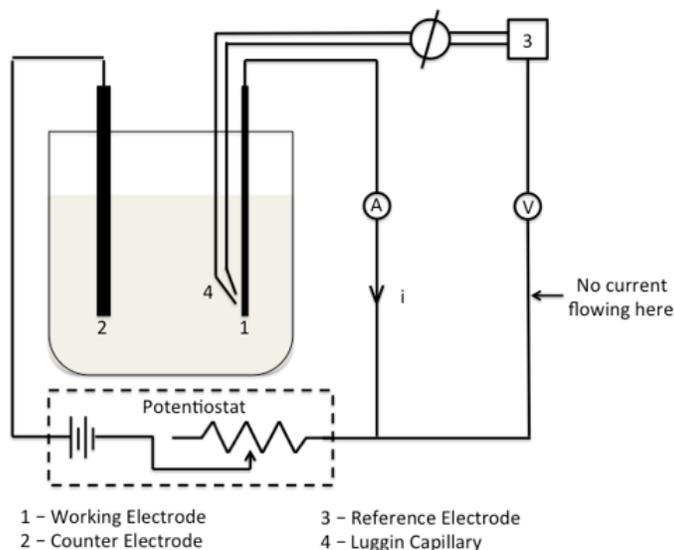


Figure 19: SCHEMATIC OF A TYPICAL THREE-ELECTRODE CELL USED FOR ELECTROCHEMICAL EXPERIMENTS

can be applied as well as measured. In electrochemical experiments, we can carry out the experiments in either constant current (galvanostatic) or constant potential (potentiostatic) modes. If the experiment is carried out in potentiostatic mode, specify the voltage between WE & RE; the potentiostat then applies a voltage such that you get a required potential between WE & RE. In electrochemical experiments, usually applied voltage, V_{app} means the voltage applied between WE & RE. The current 'i' is the current flowing through the cell.

We do not want the RE to distort the electric field between CE & WE as this causes an error in $V_{WE} - R E$. The choice of having RE outside the cell depends on the accuracy. If a microreference electrode is used, i.e. it is not significant enough to distort the electric field, it can be used in the cell as well.

When the reference electrode is placed outside the cell, a luggin capillary carrying KCl solution with Agar-Agar gel, or with a stopper cork is used.

Why only KCl is used in luggin capillary in most of the electrochemical experiments but not any acidic solutions?

Most of the electrolytes are aqueous electrolytes (water based) and suppose we use HCl, or other acids, the presence of H^+ ions in the solution causes a sort of a polarization effect (a liquid junction potential can arise). This is because the

mobility of H^+ ions is higher than the diffusivity of H^+ ions and as a result the rate of transfer of cations and anions in the solution during the electrochemical experiments is not the same. To avoid this, a salt solution like KCl maintains almost the same mobility through the luggin capillary.

How to minimize the effect of electrolyte resistance while measuring V_{WE-RE} ?

The luggin capillary has a very fine bore. Due to the fine bore (small cross-sectional area), the electrolyte resistance cannot be neglected. To avoid this effect, the luggin capillary is placed as close as possible to the working electrode.

8.1 TYPES OF ELECTROCHEMICAL EXPERIMENTS (ONLY A FEW IMPORTANT ONES ARE MENTIONED HERE)

A very broad classification of electrochemical experiments is: Steady-state measurements and transient (non-steady-state measurements).

8.1.1 STEADY STATE EXPERIMENTS

In steady state experiments, you allow the working electrode to stabilize in the solution, let the potential across the WE-electrolyte stabilize and measure the potential with RE. An example is the measurement of open circuit potential (OCP). Usually in these experiments, the electrolyte is not agitated/stirred.

8.1.2 TRANSIENT STATE EXPERIMENTS

In transient experiments, you measure the potential across the EDL of the WE by varying the current or vice versa and you carry out a mathematical analysis of the physical situation.

The different types of Transient state experiments are:

- 1) Chronopotentiometry (Galvanostatic mode): Apply a constant current and measure V_{WE-RE} with t . Typical examples are electrodeposition, also used for batteries.
- 2) Chronoamperometry (Potentiostatic mode): Apply a constant potential across WE (i.e. V_{WE-RE}) and measure current 'i' with t . Typical experiments are measurements on electrochemical batteries.

3) Linear sweep voltammetry. Apply $V_{\text{WE-RE}}$, which is varying linearly with time, and measure the current 'i' (or current density) with time and plot $V_{\text{WE-RE}}$ versus current 'i' (or usually $\log i$). Typical experiments are for corrosion experiments, cyclic voltammetry.

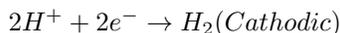
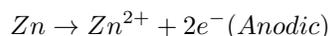
8.1.3 Applications of electrochemical methods for corrosion behaviour

POLARIZATION DIAGRAMS The polarization diagram is a plot between the potential (i.e. the thermodynamic axis) and current density (i.e. the kinetic axis). The changes in the current density as a function of polarization is represented in these polarization diagrams and several electrochemical reactions and processes can be easily understood utilizing these diagrams. The polarization diagrams are also known as Evans diagrams, based on the mixed potential theory. Electrochemical systems are defined by the parameters E^o , β_a , β_c and i_o . The postulates of mixed potential theory are:

- 1) While considering a conducting surface, the overall electrochemical reaction can be broken up into anodic and cathodic half cell reactions.
- 2) Applying charge conservation, the total rate of oxidation will be equal to the total rate of reduction. Since rates are defined by current density, the sum of anodic oxidation currents will be equal to sum of cathodic reduction currents.

While constructing the polarization diagram, the potential is represented on the y-axis and the current density on the x-axis. This implies that we are referring to the thermodynamics of an electrochemical reaction on the y-axis and current density on the x-axis. The potential is represented in a linear scale and the current density in logarithmic scale. Cathodic current densities are negative but are represented as positive in the polarization diagram.

Consider the reactions for zinc getting corroded in an acid solution. The anodic and cathodic reactions are given by



These reactions are called as the half-cell reactions and the potential corresponding to them are called cell potentials. The potentials cannot coexist separately

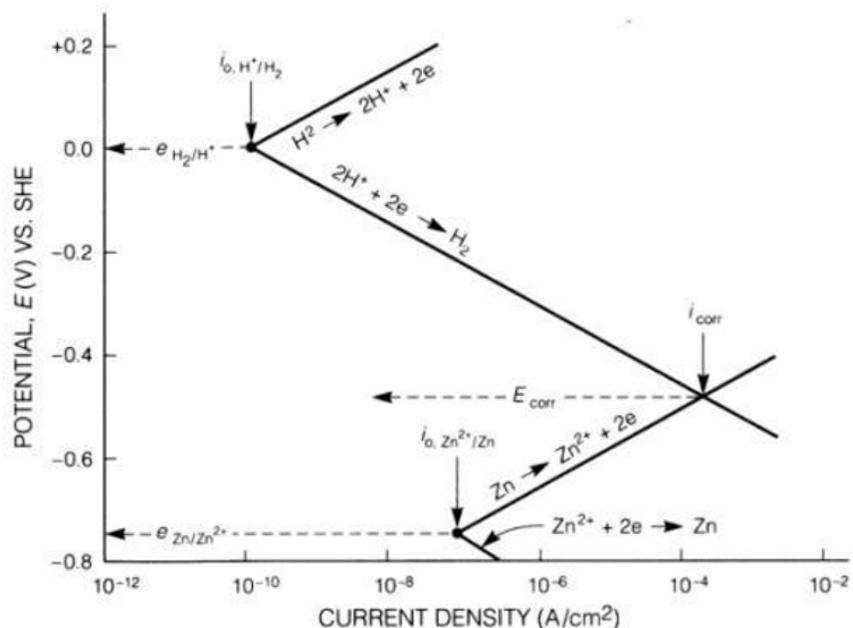


Figure 20: EVANS DIAGRAM FOR AN ACTIVE METAL (ZN)

on an electrically conducting surface. The potentials will polarize to an intermediate value called as the corrosion potential or mixed potential (E_{corr}). When there is no external current flowing into the system, then the equilibrium potential attained is called free corrosion potential (E_{corr}). As the reactions polarize on the same surface the change in potentials is given by equations [54],[55]. At E_{corr} the rate of anodic and cathodic reactions are equal and is equal to the current density, i_{corr} . The half-cell reactions for dissolution of Zn in acid are shown in the Fig. 20.

It has to be noted that the nature of the polarization diagram depends on several factors and most important of them is the dominant type of polarization. When the electrochemical reaction is in the regime of activation polarization, the curve follows the Butler-Volmer equation and for typically low values of overpotential (≤ 100 mV) the nature of curve is more or less linear. When the reaction is in the regime of concentration/diffusion polarization, the rate of reaction is limited by the concentration gradient between the electrode-electrolyte interface and bulk electrolyte, thus the rate of reaction reaches a limiting current density and the curve appears asymptotical.

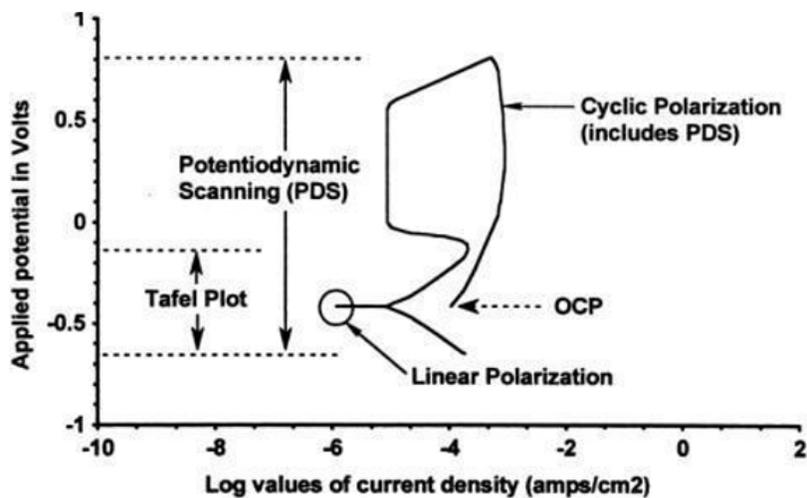


Figure 21: VARIOUS TYPES OF POLARIZATION METHODS

The polarization diagram is a plot between the potential (i.e. the thermodynamic axis) and current density (i.e. the kinetic axis). The changes in the current density as a function of polarization is represented in these polarization diagrams and several processes related to corrosion (and electrochemistry) can be easily understood utilizing these diagrams. The various polarization techniques that are commonly used are linear polarization, Tafel extrapolation, potentiostatic polarization and cyclic polarization. These four polarization techniques are summarized in the Fig.21

STABILIZATION OF POTENTIAL (OPEN CIRCUIT POTENTIAL MEASUREMENT) The variation in open circuit potential (OCP), also termed sometimes as free corrosion potential (FCP) is monitored for a period of 1 hour after immersing the working electrode in an electrolyte and measuring the potential against a standard reference electrode.

LINEAR POLARIZATION Linear polarization gives a quick estimate of the corrosion resistance and uses the smallest potential spectrum of all the DC corrosion test methods. The main advantage of linear polarization over other DC corrosion tests is that it is essentially a non destructive test because the potential spectrum is small. Linear polarization experiments are usually performed by scanning in a potential range from -20 mV to +20 mV about

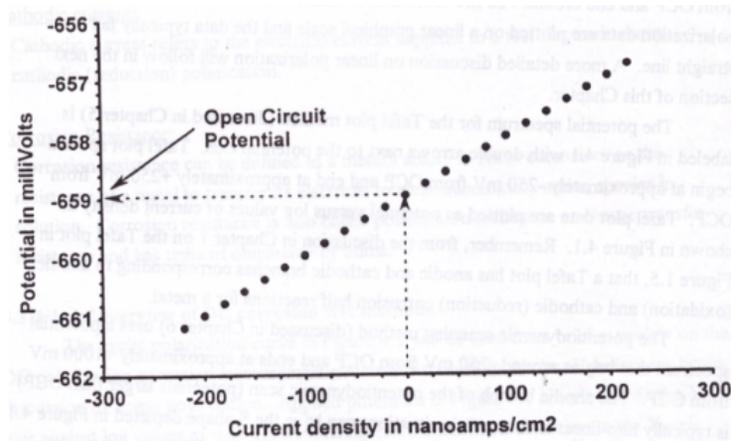


Figure 22: EXAMPLE LINEAR POLARIZATION CURVE

the free corrosion potential. A curve between potential VWE-RE and current is plotted, which is a straight line, the slope of which around OCP gives the corrosion resistance.

TAFEL POLARIZATION Tafel polarization experiments are usually performed by scanning in a potential range from -100 mV to +100 mV from the free corrosion potential. While linear polarization gives a quick estimate whether the metal has corrosion resistance, Tafel polarization gives a more elaborate estimation on the corrosion behavior of a metal in a solution. The V_{WE-RE} is plotted against the logarithm of the current density, see Fig.24 and from this plot, by extrapolating the linear regions of the anodic and cathodic curves, it is possible to estimate the corrosion potential (E_{corr}) and the rate of corrosion, i.e. corrosion current density (i_{corr}).

POTENTIODYNAMIC POLARIZATION The potentiodynamic scanning method uses a spectrum that begins around -250mV from OCP and ends at approximately +1000mV from OCP. The anodic branch of the potentiodynamic scan is typically non-linear and depends on the metal under study. A metal that corrodes actively shows one type of a curve while a metal that shows passivation has another type of a curve. An active metal corrodes aggressively and the current density keeps increasing until a limiting value is reached and looks asymptotical. An active-passive metal first starts corroding actively and once



Figure 23: EXPERIMENTAL SETUP FOR ELECTROCHEMICAL TESTS

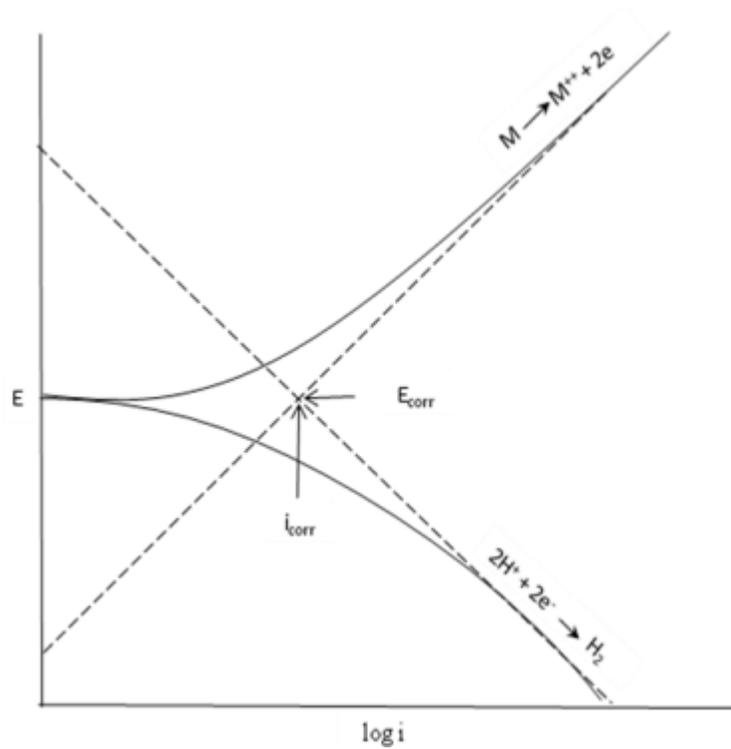


Figure 24: TAFEL POLARIZATION

a passive film starts forming, the current density decreases. When a complete protective passive film is formed, the corrosion rate (current density) reaches a minimum value.

CORROSION BEHAVIOR OF A METAL SHOWING PASSIVATION When a freshly prepared (and not oxide or surface film covered) metal surface is exposed to the aqueous environment and the anodic polarization is begun immediately on immersion. At the equilibrium reversible potential of the metal (E_{rev}), the exchange current density (i_o) depicts the rate of the forward reaction (i.e. corrosion) being equal to the rate of the reverse reaction (i.e. reduction). On anodically polarizing the material, thermodynamic conditions for the formation of a stable surface film are established at point A. Surface film is meant here in the general sense without specifying the exact nature of the film. This is because the nature of the surface film that results in passivity could be the corrosion product layer, oxide/oxyhydroxide film, adsorbed oxygen or adsorbed ions.

Different mechanisms operate in different alloy systems. On further anodically polarizing the material, the passive film nucleates on the surface from point B onwards and this indicates the potential for initiation of passivity (E_{ip}). The location of the points A and B with respect to (E_{rev}) depends upon the alloy system. On further increasing the potential, the film starts covering the surface laterally and at optimum coverage, the critical current density (i_{crit}) is achieved (point C), corresponding to which the primary passivation potential (E_{pp}) is defined. On further anodic polarization beyond (E_{pp}), the surface passive film completely covers the surface and the current density decreases with increasing anodic polarization until the point D, when the passive film completely covers the surface. The potential corresponding to point D is referred to as the potential for complete passivation (E_{cp}). Therefore, in the region where there is a fall in current density, this implies that the surface is getting covered up with a surface film that hinders the corrosion of metal.

Once complete coverage is achieved at point D, further polarization of the metal leads to growth of the passive film visually on the polarization diagram, on polarizing past this potential, the current density remains constant with increasing potential in the passive range (Fig. 25). This region is known as the passive range.

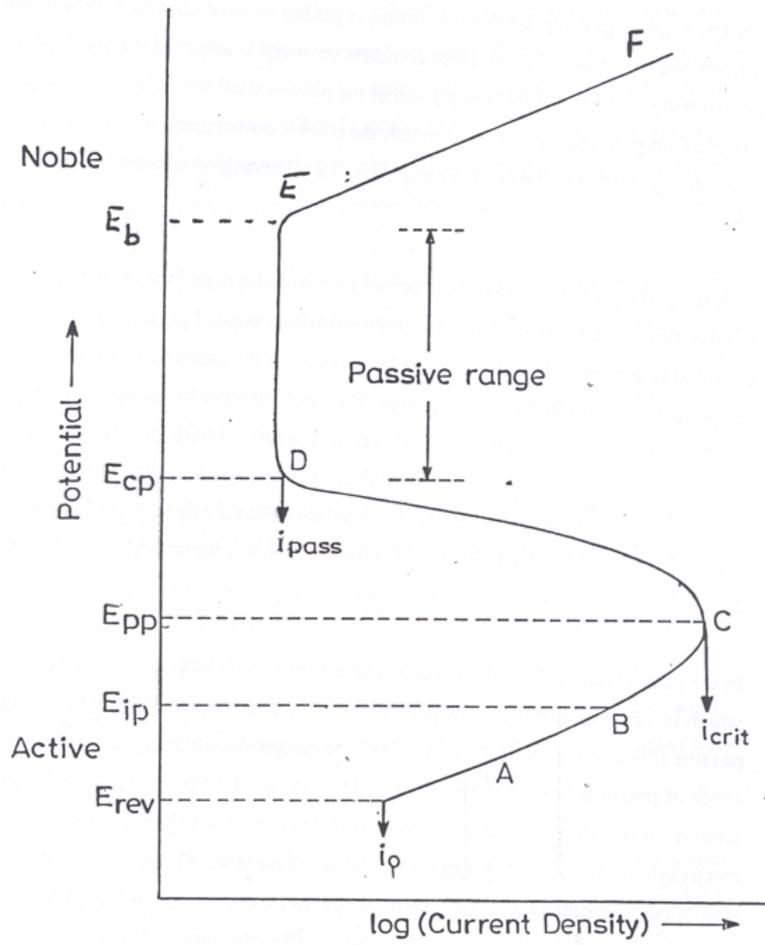


Figure 25: CORROSION BEHAVIOR OF A METAL SHOWING PASSIVATION

This is the region that has to be viewed carefully in order to understand the nature of passive film on the surface. How does the increasing potential get accommodated? The potential is accommodated by increase in thickness of the passive film on polarizing in the anodic direction in the passive region. The ions that enter the passive film lattice move towards the solution interface and this results in growth of the passive film. The higher film thickness helps maintain a high electric field gradient within the film. There will be some corrosion of ions going into solution from the other side of the passive film exposed to the solution and this rate of corrosion is that is indicated by the passive current density, i_{pass} . In the passive region, the current density remains constant with increasing anodic polarization, which is due to thickening of the passive film. It is important to note the fine dimensions of the passive films. The current density remains constant over a significant range of potential in the passive range, and this is called the passive current density (i_{pass}).

The passive current density is dictated by the constant rate of dissolution of the metal ions into the electrolyte from the passive film surface. Thickening of the film accommodates the increasing anodic positive potentials in the passive range. In case the potential is held constant in the passive range after the formation of the passive film, the current density decreases with time. This has generally been modeled by logarithmic growth kinetics. Therefore, the time factor is also an important consideration while discussing passivation. On further anodically polarizing the material, several reactions can lead to the destruction of passivity (i.e. indicated by increasing current density with increasing potential). Some of these processes are oxygen evolution, transpassive dissolution due to conversion of the passive film forming ion to a higher oxidation state, pitting caused by destabilization of the passive film due to the presence of halide ions or changes in the nature of the passive film (for example anodizing wherein there is a change in porosity of the passive film). Passivity can be very effectively broken down due to the presence of certain ions in solution. One of the most dangerous is chloride ions. In general, all the halide ions are prone to cause passivity breakdown. Normally, breakdown due to halide induced attack occurs at potentials much lower than the other processes described above. Therefore, there is an effective drastic fall in the passive range in the presence of halide ions.

Current Distribution	Assumptions	Parameters
Primary	Absence of overvoltages	Geometry (Cell, Electrodes)
Secondary	Activation overvoltage without concentration variations near the electrode	Geometry, activation overvoltage, conductivity of electrolyte and electrodes
Tertiary	Activation and concentration overvoltages	Geometry, conductivity, activation and concentration overvoltages

Figure 26: TYPES OF CURRENT DISTRIBUTION AND PARAMETERS AFFECTING IT

9 CURRENT DISTRIBUTION

Current distribution is very important parameter in electrochemical cells. The main factors that affect influence current distribution are geometry of the cell system, conductivity of the electrolyte and electrodes, activation overpotential at the electrodes, which depends on the electrode kinetics, and concentration overpotential that is controlled by mass transport processes. Depending on one these factors taken into account, three kinds of current distribution Primary, Secondary and Tertiary current distribution can be distinguished as shown in Fig.26. Primary current distribution depends on cell geometry and is independent of electrochemical parameters. Therefore, the primary current distribution would be not be affected by the applied current waveform. It is generally dependent on the electrolyte resistance.

The secondary current distribution arises due to the effects of activation overpotential. In general, the secondary current distribution is more uniform than the primary or tertiary current distribution. The resistance of cathode surface is much less than that of the electrolyte. Therefore, the cathode can be considered to be an equipotential surface. This tends to counteract the effect of irregular geometry. This can be illustrated by regarding the activation overvoltage as the result of a so-called polarization resistance which is the first derivative of the overpotential with respect to the current density and which represents in fact a resistance per unit area.

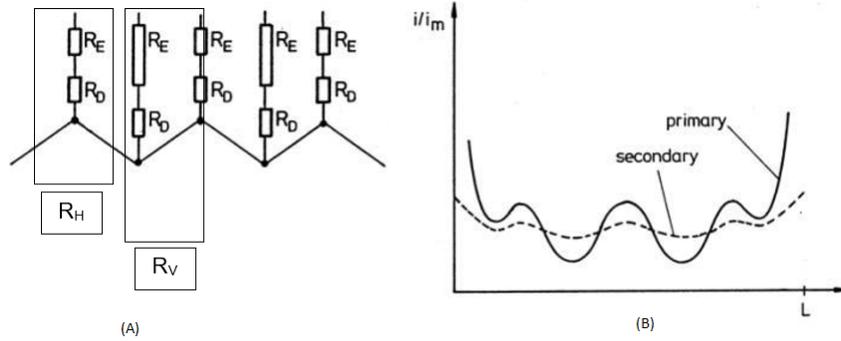


Figure 27: (A) SERRATED ELECTRODE PROFILE WITH ELECTROLYTE AND POLARIZATION RESISTANCES IN SERIES, (B) SCHEMATIC DRAWING OF THE PRIMARY AND SECONDARY CURRENT DISTRIBUTION ON A SERRATED ELECTRODE

$$R_p = \frac{d\eta}{di}$$

In Fig.27 (a), the electrolyte resistance and the resistance due to the double layer are given by R_E and R_D respectively. The serrated surface profile shows clearly that the electrolyte resistance to the peaks (R_h) is smaller than that to the valleys (R_v). If the overvoltages are neglected, according to Kirchoff's law the ratio between peak and valley current density is given as

$$\frac{i_h}{i_v} = \frac{R_v}{R_h} > 1$$

If an additional polarization resistance R_p is taken into account in series to the electrolyte resistance, then the current density ratio is modified to

$$\frac{i_h}{i_v} = \frac{R_v + R_p}{R_h + R_p} < \frac{R_v}{R_h}$$

resulting in a more uniform current density distribution as shown schematically in Fig.27 (b). The secondary current distribution is an important consideration in electrodeposition because it is known that the secondary current distribution should result in uniform plating.

The tertiary current distribution arises due to the effects of all three kinds of polarization, namely activation, concentration and resistance overpotential. In

case of tertiary current distribution, one takes into account an additional concentration overvoltage, which is usually a diffusion overvoltage. This occurs when the current density is limited by the mass transport rate through the diffusion layer. For a serrated electrode profile, two extreme cases are illustrated by Fig.28. In the case of the so-called macroprofile (Fig.28 (a)), the diffusion layer thickness is small as compared to the electrode roughness and the diffusion resistance enhances the polarization resistance resulting in a more uniform current distribution than the secondary one. If the electrode roughness is small compared to the diffusion layer thickness (Fig.28 (b)) then the peaks are better accessible to diffusion layer than valleys.

This means that the highest current densities are obtained at the peaks. Now if a diffusion limited deposition takes place then the highest deposition rates are given at peaks. This means that the surface roughness will be enhanced. In an extreme case a dense metal deposition is no longer possible and the deposited metal breaks out of the surface and this is utilized for electrochemical metal powder production.

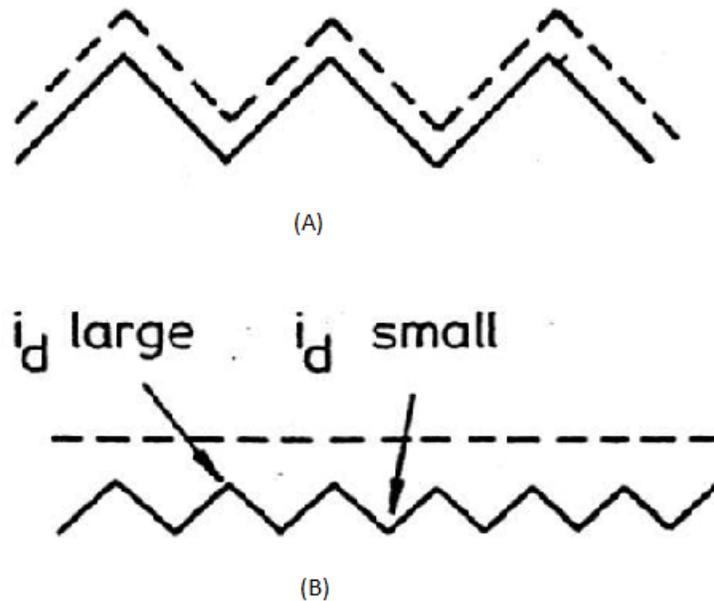


Figure 28: SERRATED ELECTRODE PROFILE WITH DIFFUSION LAYER:(A) MACROPROFILE, (B) MICROPROFILE

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