2.0 Activation Overpotential

Chapter 2 starts with a discussion on the electric double layer and its effect on activation overpotential. It will be followed by the derivation of the Butler-Volmer equation that describes the relationship between activation overpotential and current density. Finally, the concept of polarization will be explained. Worked examples are given at the end of the chapter.

2.1 Electric Double Layer

Recall the discussion on the origin of half-cell potential. There it was shown that if a metal electrode is dipped in a solution of its ions, two parallel layers of charge form on both the electrode and electrolyte side of the interface. This parallel layer of charge is known as the electric double layer (EDL). In reality, the structure of the EDL is more complicated. A layer of solvent, for example, water molecules is electrostatically attached to the negatively charged electrode, as shown in Fig. 1. Next to the water molecules, there is a layer of specifically adsorbed ions, not shown in the figure, the locus of the centres of which is called the inner Helmholtz plane (IHP). Beyond, the IHP, the counter-ions (negative charge) are located parallel to the positive charge on a plane called the Outer Helmholtz Plane (OHP). The OHP is located at a distance of approximately 1 nm from the electrode. However, the thermal energy of the electrolyte causes some negative ions to break away from the OHP and distributed randomly in a region extending up to the bulk electrolyte; this region is called the diffuse double layer (DDL).

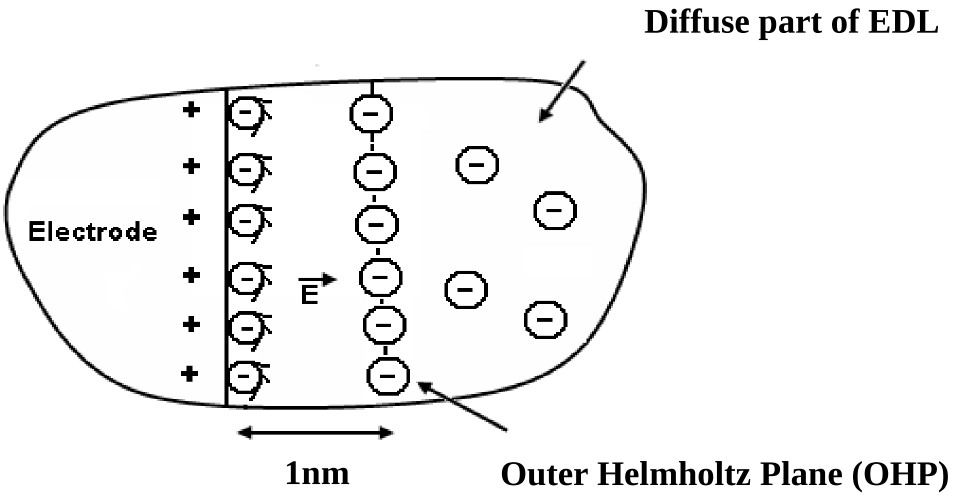

Fig. 2.1. Schematic diagram of an electric double layer at the electrode/electrolyte interface

Fig. 2.2 shows the voltage profile in the EDL. The voltage drop is linear between the electrode and the OHP, and then asymptotically goes to zero at the edge of the DDL. The bulk electrolyte region starts beyond the DDL. It was pointed earlier that there is no separation of charge in the bulk electrolyte, as the condition for electroneutrality holds here.

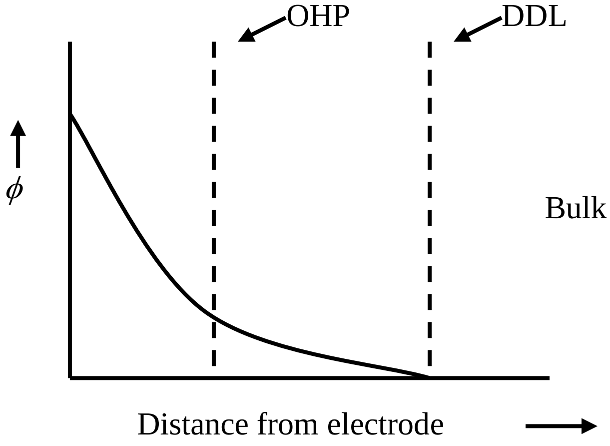

Fig. 2.2. Voltage profile across the electric double layer.

To simplify the analysis of electrochemical kinetics, the DDL can be neglected and it can be assumed that the EDL extends up to the OHP. Consequently, the electrode/electrolyte interface can be thought of as a capacitor, with the electrode side of the interface and the OHP being the oppositely charged plates, and the solvent being the dielectric. Hence the potential drop at the electrode/electrolyte interface at equilibrium is defined as:

$\Delta\phi_e$ = potential drop across EDL at equilibrium
= reduction potential of the half cell reaction (E^o)

What happens when the above electrode is hooked up as a part of an electrolytic cell? Let us assume that the electrode becomes an anode and a current is passing through the cell. That is, an anodic reaction such as $Zn \rightarrow Zn^{2+} + 2e$ is taking place at the anode. Under these circumstances, the potential drop in the EDL will change from $\Delta\phi_e$ to a more positive value $\Delta\phi$, which will become more positive with increasing current, or more specifically, current density at the anode. Similarly, at the cathode, for the reaction $Cu^{2+} + 2e \rightarrow Cu$, the potential drop in the EDL will change from $\Delta\phi_e$ to a more negative value $\Delta\phi$, which will become more negative with increasing current. Hence in general, when a current flows through a cell, $|\Delta\phi| > |\Delta\phi_e|$ for the EDLs adjacent to both the anode and the cathode.

One way of understanding the sign of $\Delta\phi$ is to do a thought experiment on the electrowinning of copper. Here, voltmeters are connected to measure the potential between anode and cathode ($\Delta\phi_{ac}$), anode and ground ($\Delta\phi_a$), and cathode and ground ($\Delta\phi_c$) during electrolysis. The corresponding equilibrium potentials, that is when no current is passing though the cell, are $\Delta\phi_{ac0}$, $\Delta\phi_{a0}$, and $\Delta\phi_{c0}$. With increase in current flowing through the cell, if we increase current with time, we will observe that (i) $\Delta\phi_{ac}$ will increase with time, that is, $(\Delta\phi_{ac} - \Delta\phi_{ac0}) > 0$, (ii) $\Delta\phi_a$ will increase with time, that is, $(\Delta\phi_a - \Delta\phi_{a0}) > 0$, and (iii) $\Delta\phi_c$ will decrease with time, that is, $(\Delta\phi_c - \Delta\phi_{c0}) < 0$. At all times during the experiment, $\Delta\phi = \Delta\phi_a - \Delta\phi_c$.

2.2.1 Importance of the electric double layer

The voltage drop across the EDL is ~ 1 V. Since the thickness of the EDL is of the order of 1 nm, the electric field across the double layer is extremely large (10^9 V/m). The importance of the double layer arises from the fact that the electric field in the EDL can either accelerate or decelerate an ionic species involved in a half cell reaction. For example, if the electrode in Fig. 2.1 becomes an anode then the direction of the electric field is towards the cathode. Hence for the reaction $\boldsymbol{Fe^{2+} \rightarrow Fe^{3+} + e}$ to occur, work must be done to transport $\mathbf{Fe^{2+}}$ through the EDL so that it can reach the electrode where the above half cell reaction can take place. Now assume that the anode in Fig. 1 is made of Zn and the following reaction takes place: $\boldsymbol{Zn \rightarrow Zn^{2+} + 2e}$. Now Zn^{2+} has to be transported away from the anode; the motion of Zn^{2+} is aided by the electric field. That is, the electric field $\vec{E}$ hinders the motion of positive ion towards the anode and favours the motion of positive ion away from the anode. A similar argument can be made for negative ions at the anode. The effect of the electric field of the EDL at the cathode on the motion of the ions can be reasoned similarly.

Point of caution: The motion of ion should always be thought of with respect to the direction of the electric field and not the electrode polarity. You will see later that electrowinning and galvanic cells have opposite polarity conventions.

Hence we see that activation overpotential consists of two components:

- Electrical energy associated due to the Interaction between ion & $\vec{E}$
- Activation energy of the charge transfer reaction, as in any chemical reaction.

An important parameter in characterizing activation potential is current density, *i*. In an electrolysis cell, I is always constant, but "*i*" for the anode and cathode will differ if their submerged areas differ[1]. In electrochemical kinetics, "*i*" is more important than I, the latter being used primarily to determine the rate of half cell reactions at the electrodes, for example, metal deposition/dissolution rates or gas evolution rates. As shown in Chapter 1, to determine V_{cell}, for a given current, in electrolytic cells, a quantitative relationship between activation overpotential (η_a) and current density has to be specified for the half-cell reactions occurring at both electrodes. The Butler-Volmer equation (BVE) relates η_a to *i* and is derived in the next section.

2.2 The Butler-Volmer equation

Let us consider the following half-cell reaction $P^{n+} + ne = Q$.

Define,
$C_{P^{n+}}$ = Concentration of P^{n+} at the electrode/electrolyte interface
$C^*_{P^{n+}}$ = Bulk concentration of P^{n+}
C_Q = Concentration of Q at the electrode/electrolyte interface
C^*_Q = Bulk concentration of Q

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[1] Consider the case when a 1m^2 flat plate is ground to fine pieces, with an average size of 0.5 mm. Clearly the total surface area of the ground pieces would >> 1 m^2. If we operate a cell with a 1 m^2 flat anode and a particulate cathode, made by grinding a 1 m^2 flat plate, then $i_c << i_a$.

Q can either be an ion such as Fe^{2+} or a metal such as Cu. If Q is a metal, then C_Q and C_Q^* refer to the concentration of an intermediate soluble species of the metal, which finally oxidizes to yield the corresponding metal ion.

At equilibrium, that is when no current is passing through the cell, $C_{P^{n+}} = C^*_{P^{n+}}$. In other words, the concentration of P^{n+} is uniform throughout the electrolyte. However, when current passes through the cell, there is a net half-cell reaction taking place at the electrode, which would result in $C_{P^{n+}} \neq C^*_{P^{n+}}$. For example, if we focus at the cathode $\boldsymbol{A^{n+}}$ is being consumed, we will find that $C_{P^{n+}} < C^*_{P^{n+}}$.

For deriving the BVE, we focus at one electrode; it could either be the cathode or the anode. The half-cell reaction $\mathbf{P^{n+}}$ + ne = Q is actually composed of two reactions:

$$P^{n+} + ne \rightarrow Q \tag{2.1}$$

$$Q \rightarrow P^{n+} + ne \tag{2.2}$$

At equilibrium, the rates of both reactions 2.1 and 2.2 are identical meaning there is no net reaction taking place. If the half cell reaction P^{n+} + ne = Q occurs at the anode then the rate of reaction 2.2 will be greater than the rate of reaction 2.1. Similarly, if the half-cell reaction occurs at the cathode then the rate of reaction 2.1 will be greater than the rate of reaction 2.2. Before proceeding further we have to give a precise meaning to the “rate of a half-cell reaction.”

The rate of reaction (1) can be defined in terms of either the rate of consumption of P^{n+} or the rate of production of P. We normally prefer to define rate of reaction in terms of current density at the electrode. For example, in copper electrowinning, we would define rate in terms of Cu^{2+}. To define the rate of consumption of P^{n+} ions, conduct a mass balance on a small control volume adjacent to the cathode (see Fig. 2.3). The left face of the control volume is slightly inside the cathode.

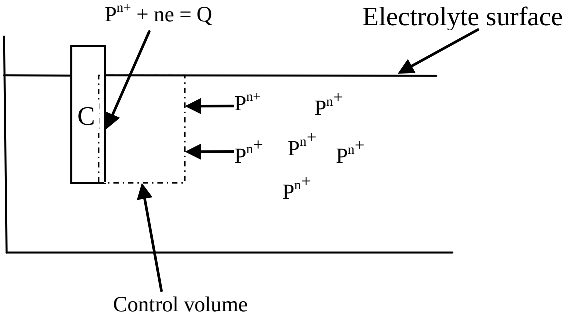

Fig. 2.3. Mass balance of P^{n+} over a control volume adjacent to the cathode.

Rate of accumulation of P^{n+} in the control volume = Rate of inflow of P^{n+} in the control volume
(a) (b)
- Rate of outflow of P^{n+} in the control volume - Rate of consumption of P^{n+} in the control volume
(c) (d)
by electrochemical reaction[2] (2.3)

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[2] If P^{n+} is generated by an electrochemical reaction, for example reaction 2, term (d) will now become (+ Rate of generation of P^{n+} in the control volume by electrochemical reaction).

Under steady state conditions, term (a) = 0. Since P^{n+} cannot penetrate the electrode, term (c) is zero. P^{n+} is simultaneously flowing into control volume from the bulk electrolyte and consumed by reaction (1), therefore terms (c) and (d) are non-zero. Equation 2.3 therefore reduces to:

Rate of consumption of P^{n+} in the control volume by electrochemical reaction = Rate of inflow of P^{n+} in the control volume (2.4)

That is, rate of consumption of P^{n+} can be defined with respect to the flux of P^{n+}, N_c, from the bulk electrolyte to the cathode.

It is more convenient to define the rate of reaction in terms of the current density at the electrode because it can be easily determined. Let us assume that for a current I A, P^{n+} ions are being transported from the bulk electrolyte to the cathode at the rate of N_cA_c mol/s. Now, one mole of P^{n+} contains nF coulombs of charge. Thus, equating the charge associated with the rate of inflow of P^{n+} ions and electron flow rate, we get:

$$I = nFN_cA_c \tag{2.5}$$

where,
n = number of electrons participating in the half-cell reaction.
F = Faraday's constant.
N = Flux of ionic species involved in the half-cell reaction ($mol.m^{-2}.s^{-1}$).

Dividing equation 2.5 throughout by A_c, we get[3]:

$$i_c = nFN_c \tag{2.6}$$

Assume i_c and i_a are current densities that are proportional to the rate of the cathodic (reaction 1) and anodic (reaction 2) reactions. At equilibrium, $i_c = i_a$. If the electrode is an anode, define $i = i_c - i_a < 0$. Similarly, if the electrode is a cathode, $i = i_c - i_a > 0$.

Now consider that a cathodic reaction is taking place at the electrode, that is, we are consuming P^{n+} and producing Q. The BVE relates i to η_a through an expression for the rate of reaction. We will assume that the electric field in the EDL is directed from the electrode towards the bulk electrolyte[4].

Doing a mass balance on P^{n+} at a unit area of the electrode/electrolyte interface, assuming first that the reaction $P^{n+} + ne \rightarrow Q$ is taking place in the forward direction:

Rate of transport of P^{n+} from the bulk electrolyte to the electrode = Rate at which P^{n+} is being consumed by the half cell reaction[5]. Thus:

$$N_c = \frac{kT}{h} C_{P^{n+}} e^{\frac{-\Delta G_{ec}}{RT}} \tag{2.7}$$

Here N_C is the flux of P^{n+}. Please recall that the RHS of equation 2.7 is similar to the expression of a first order chemical reaction. The electrochemical potential ΔG_{ec} is defined as[6]:

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[3] In a similar manner, current density at the anode can be defined with respect to the flux of the ion involved in the anodic half-cell reaction.

[4] We could have well assumed that the electric field was directed from the bulk electrolyte towards the electrode without changing the expression of the BVE.

[5] Readers are referred to Bard for a detailed discussion on the origin of equation 2.7.

[6] Readers are referred to Bockris and Reddy, Bard or any standard text book on thermodynamics for a detailed discussion on ΔG_{ec}

$$\Delta G_{ec} = \Delta G_c^* + \beta nF\Delta\phi \tag{2.8}$$

ΔG_c^* = Activation energy for the cathodic reaction ($P^{n+} + ne \rightarrow Q$) per mole of P^{n+}
$\beta nF\Delta\phi$ = Work done by the ion P^{n+} to overcome the electric field $\vec{E}$ of the EDL, which, for this reaction, opposes the motion of P^{n+} towards the electrode. β is called the "symmetry factor" and usually equals 0.5.

Substituting equation 2.8 in equation 2.7, we get:

$$N_c = k_{cc}C_{P^{n+}}e^{\frac{-\beta nF\Delta\phi}{RT}} \tag{2.9}$$

or,

$$i_c = nFN_c = nFk_{cc}C_{P^{n+}}e^{\frac{-\beta nF\Delta\phi}{RT}} \tag{2.10}$$

Similarly for the anodic reaction, $Q \rightarrow P^{n+} + ne$

$$\Delta G_{ec} = \Delta G_c^* - (1-\beta)nF\Delta\phi \tag{2.11}$$

The negative sign before the second term in equation 10 signifies that now the electric field in the EDL aids the motion of P^{n+} from the electrode to the bulk electrolyte, there by reducingΔG_{ec}. Equation 2.11 finally reduces to:

$$i_a = nFk_{ca}C_Qe^{\frac{(1-\beta)nF\Delta\phi}{RT}} \tag{2.12}$$

At equilibrium, that is, when the rates of the $P^{n+} + ne \rightarrow Q$ and $Q \rightarrow P^{n+} + ne$ of the reactions are equal[7], and there is no net flow of current:

$$C_{P^{n+}} = C_{P^{n+}}^* \tag{2.13}$$

$$C_Q = C_Q^* \tag{2.14}$$

and,

$$i_o = i_a = i_c = nFk_{cc}C_{P^{n+}}^*e^{\frac{-\beta nF\Delta\phi_e}{RT}} = nFk_{ca}C_Q^*e^{\frac{(1-\beta)nF\Delta\phi_e}{RT}} \tag{2.15}$$

i_o is the exchange current density, which represents the kinetics of a half-cell reaction. Equation 2.15 shows that i_o is a function of concentration of the electroactive species, the magnitude of the half-cell potential and temperature. In simple terms, i_o is proportional to the rate of the forward and backward reaction at equilibrium and is the critical parameter that characterizes activation overpotential.

Table 2.1 lists typical values of i_o for different half-cell reactions/electrode/electrolyte combinations.

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[7] Here, $i_a = i_c$

Table 2.1. i_o for different half-cell reactions/electrode/electrolyte combinations.

Electrode	**Reaction**	**Electrolyte**	**i_o ($A.m^{-2}$) at 25°C**
Pt	Ce^{4+}/Ce^{3+}	H_2SO_4	0.4
Pt	Fe^{3+}/Fe^{2+}	H_2SO_4	25.1
Rh	Fe^{3+}/Fe^{2+}	H_2SO_4	17.4
Pt	H^+/H_2	H_2SO_4	7.9
Hg	H^+/H_2	H_2SO_4	7.9×10^{-9}

What do we observe about i_o from Table 2.1?

- For the same electrode, i_o is a function of the half-cell reaction.
- For the same half-cell reaction, i_o can be a function of the electrode material; this dependence is more significant for gas evolution reactions.

From experiments, we know that it is extremely easy to evolve H_2 by the reaction $2H^+ + 2e = H_2$ on a platinum cathode[8], while it is virtually impossible to evolve H_2 on a mercury cathode. In fact, platinum is closest to an ideal non-polarizable electrode for H_2 (gas) evolution reaction; that is, in general:

- Low $i_o \Rightarrow$ slow reaction kinetics
- High $i_o \Rightarrow$ fast reaction kinetics

FFT: i_o cannot be measured with an ammeter. Why?

Let us now consider the non-equilibrium case, that is, when there is a flow of current[9]. Under non-equilibrium conditions, the potential drop across the double layer changes from $\Delta\phi_e$ to $\Delta\phi$.

$$i = i_c - i_a = nFk_{cc}C^*_{P^{n+}}e^{\frac{-\beta nF\Delta\phi}{RT}} - nFk_{ca}C^*_Q e^{\frac{(1-\beta)nF\Delta\phi}{RT}} \tag{2.16}$$

Define,

$$\text{Overpotential } \eta = \Delta\phi - \Delta\phi_e \tag{2.17}$$

Please note $\Delta\phi_e$ = Reduction potential of the half-cell reaction, $P^{n+} + ne \rightarrow Q$. As described earlier, the sign of η is positive for an anodic reaction and negative for a cathodic reaction.

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[8] The phrase "easy to evolve" is related to polarizability, which will be formally defined in a later section of this chapter.

[9] The electrode will be a cathode for $i > 0$ and an anode for $i < 0$.

Substituting equation 2.17 in equation 2.16, we get:

$$i = \left\{nFk_{cc}C^*_{P^{n+}}e^{\frac{-\beta nF\Delta\phi_e}{RT}}\right\}\frac{C_{P^{n+}}}{C^*_{P^{n+}}}e^{\frac{-\beta nF\eta}{RT}} - \left\{nFk_{ca}C^*_Q e^{\frac{(1-\beta)nF\Delta\phi_e}{RT}}\right\}\frac{C_Q}{C^*_Q}e^{\frac{(1-\beta)nF\eta}{RT}} \tag{2.18}$$

Substituting equation 2.15 in equation 2.18 results in:

$$i = i_o\left\{\frac{C_{P^{n+}}}{C^*_{P^{n+}}}e^{\frac{-\beta nF\eta}{RT}} - \frac{C_Q}{C^*_Q}e^{\frac{(1-\beta)nF\eta}{RT}}\right\} \tag{2.19}$$

Equation 2.19 is the **generalized** Butler-Volmer equation since it includes mass transfer effects. In equation 2.19, η represents the total overpotential, that is, it incorporates both activation and concentration overpotential. The concentration overpotential component of η arises because $C_{P^{n+}} \neq C^*_{P^{n+}}$ and $C_Q \neq C^*_Q$.

To derive an exclusive relationship for activation overpotential, one has to assume that the mass transfer of ions between the bulk electrolyte and the OHP is much faster than the rate at which the ions are reacting at the electrodes. Or, in other words, $C_{P^{n+}} \approx C^*_{P^{n+}}$ and $C_Q \approx C^*_Q$. Equation 2.19 then reduces to the more familiar form of the Butler-Volmer equation:

$$i = i_o\left\{e^{\frac{-\beta nF\eta_a}{RT}} - e^{\frac{(1-\beta)nF\eta_a}{RT}}\right\} \tag{2.20}$$

In equation 19, the first and second terms on the right hand side represent the rates of the cathodic and anodic parts of the half cell reaction (P^{n+} + ne = Q) given by equations 2.1 and 2.2. Please remember that the sign of η_a is positive for an anodic reaction and negative for a cathodic reaction. η_a is also known as the current producing potential because, as shown in equation 2.20, η_a= 0 results in i = 0, which corresponds to the half cell reaction being at equilibrium. ***In essence, activation polarization for each half-cell reaction is characterized by specific combinations of i_o and β, which are determined from experiments.***

It is important to understand that even though the Butler-Volmer equation was derived for one half cell reaction, it is applicable to all reactions taking place at the anode and the cathode. For example, in zinc electrowinning, hydrogen evolution occurs along with zinc deposition; both reactions are characterized by their respective ***i_o and β***.

2.2.1 Simplifications of the Butler-Volmer Equation (BVE)

The BVE equation is unwieldy to use in the form given in equation 19. Hence it is simplified for two important cases, namely conditions during electrolysis related to (i) large overpotentials, that is $|\eta_a| > 100\,mV$ and (ii) small overpotentials, that is, $|\eta_a| < 10\,mV$. The large overpotential approximation is generally applicable to industrial electrolysis processes such as electrowinning of metals from aqueous or molten salts.

Large overpotential approximation ($|\eta_a| > 100\,mV$)
Consider a net cathodic reaction such as the deposition of copper at the cathode. Here, the sign of η_a is negative, which means that the second term in equation 2.20 can be neglected[10]:

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[10] Explain why the second term in equation 2.20 is neglected for a cathodic reaction. Hint: The magnitude of $\eta_a$is same for both terms.

$$i = i_o e^{\frac{-\beta n F \eta_a}{RT}} \tag{2.21}$$

or,

$$\log i = log i_o - \frac{\beta n F \eta_a}{RT} \tag{2.22}$$

Equation 2.22 can also be re-written as:

$$\eta_a = \text{a} + \text{b} \log \boldsymbol{i} \tag{2.23}$$

In equation 2.23, a and b are constants, expressions for which can be determined from equation 2.22; their values are measured **experimentally**, as will be shown shortly. Each of the **equations 2.21 to 2.23** are referred to as **Tafel equation.** While using it just remember, that it is applicable only when $|\eta_a| > 100\,mV$.

Caution: While using Tafel equation for cathodic half-cell reaction, please use a negative value ofη_a.

How do we simplify the BVE for large anodic overpotentials? Remember to first use a positive value ofη_a, which means that the first term in equation 2.20 should be neglected and the resulting equation will be:

$$i = -i_o e^{\frac{(1-\beta) n F \eta_a}{RT}} \tag{2.24}$$

The negative sign only means that the direction of anodic current is opposite to a cathodic current. What is of interest is the magnitude of current and hence you can ignore the negative sign of current for all further calculations. Again, when using equation 2.24, please use a positive value ofη_a.

Low overpotential approximation ($|\eta_a| < 10\,mV$)
Here neither of the terms in equation 2.20 can be neglected. Ignoring the second and higher terms on expanding both the cathodic and anodic terms in equation 2.20, we get:

$$i = i_o \left\{1 - \frac{-\beta n F \eta_a}{RT}\right\} - i_o \left\{1 + \frac{(1-\beta) n F \eta_a}{RT}\right\} \tag{2.25}$$

or,

$$i = -\frac{i_o n F \eta_a}{RT} \tag{2.26}$$

Equation 2.26 should be used for both cathodic and anodic half-cell reactions with the appropriate sign of η_a.

Value of "n" in the Butler-Volmer Equation
Express all reactions in terms of one mole of the "relevant" ion to get the number of electrons, n.

- The hydrogen evolution reaction, $2H^+ + 2e = H_2$ becomes $H^+ + e = 0.5H_2$, which means **n = 1**
- The oxygen evolution reaction, $2H_2O = 4H^+ + O_2 + 4e$ becomes $0.5H_2O = H^+ + 0.25O_2 + e$, which means **n = 1.**
- For the copper deposition reaction, $Cu^{2+} + 2e = Cu$, **n = 2**.

2.2.2 Experimental scheme to determine i_o and β

Consider the cathodic reaction: $Cu^{2+} + 2e = Cu$

Use a three-electrode system shown in the figure below:

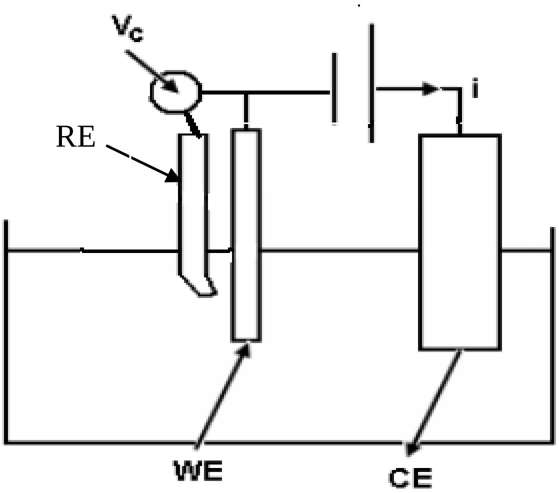

Fig. 2.4. Three electrode system used for measuring i_o and β. WE, CE, and RE and working, counter, and reference electrodes respectively.

Fig. 2.4 shows a three electrode experimental set-up that is used for determining i_o and β, details of which will be described in the chapter on experimental techniques. Briefly, three electrodes are referred to as working, counter, and reference electrodes. The reaction of interest occurs at the working electrode, which, in the present case, is the cathode. Counter electrode, for copper deposition, that is, the anode. Potential at the working electrode is measured with respect to the reference electrode; this potential is referred to as V_c, and is equal to the potential drop across the EDL of the working electrode.

In the experiment, vary the current I flowing through the cell and measure the corresponding V_c, the results of which are given in Table 2.2 below:

Table 2.2. Experimental data obtained from the 3-electrode set-up in Fig. 2.4.

Current (I, A)	Current density at the working electrode (i, A/m^2)	Voltage drop between working and reference electrodes (V_c, V)	Activation overpotential $\left(\eta_a = V_c - E_{Cu^{2+}/Cu}, V\right)$
I_1	i_1	V_{c1}	η_{a1}
I_2	i_2	V_{c2}	η_{a2}
I_3	i_3	V_{c3}	η_{a3}
I_4	i_4	V_{c4}	η_{a4}

Let us say, $|\eta| > 100$ mV in the above table, which means that the Tafel equation, as in equation 2.22 applies. Plot i versus η_a data from Table 2.2. From the resulting best-fit straight line, we get:

$$\text{y-intercept} = \log i_o \quad \text{and} \quad \text{slope} = \frac{-\beta nF}{2.303RT} \tag{2.27}$$

Hence i_o and β can be determined. n=2 for the copper deposition reaction.

2.3 Polarization Diagrams

Polarization diagrams are graphical representation of the Butler-Volmer equation and help immensely in understanding the dynamics of electrochemical reactions. For example, we can, at a constant current, directly read values of overpotentials and cell voltage. Or, for that matter, when there are more than one half-cell reactions, we can get an estimate of the current efficiency. Since we are mostly interested in large overpotential, the polarization diagram represents Tafel equation.

The polarization diagram for copper electrowinning is shown in Fig. 2.5.

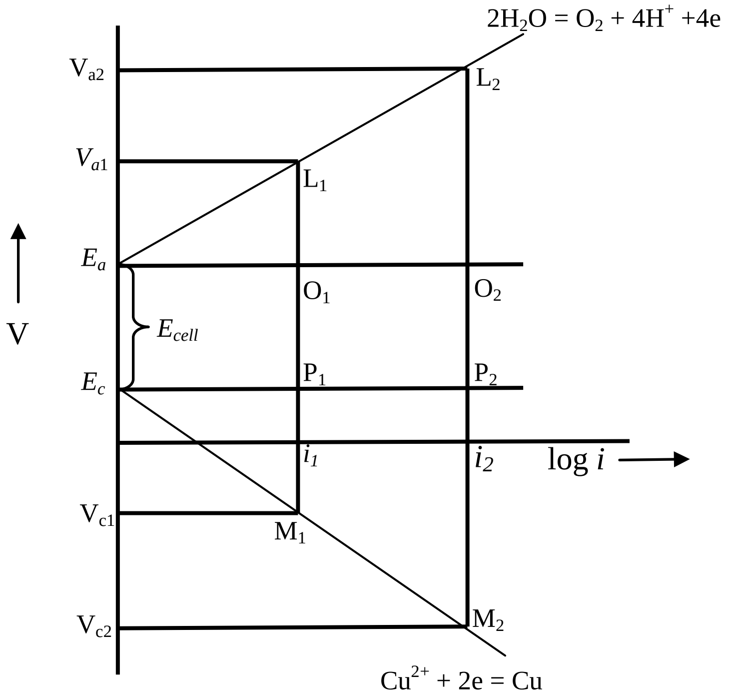

Fig. 2.5. Polarization diagram for half-cell reactions in copper electrolysis.

In the literature, the y axis in Fig. 2.5 is normally referred to as "*E*." However, I have used "*V*" because "*E*" in electrochemistry normally refers to the equilibrium half-cell potential, that is, the potential when there is no current flowing through the cell. Since this is not the case here, I have used "*V*" to denote the y axis.

In Fig. 2.5, E_a and E_c are the (equilibrium) reduction potentials for the anodic and cathodic reactions respectively. Consequently, the currents corresponding to E_a and E_c must be equal to the exchange current density for the anodic ($i_{o,a}$) and cathodic ($i_{o,c}$) reactions respectively. In most cases, $i_{o,a}$ and $i_{o,c}$ are not equal; in fact, they may be different by several orders of magnitude. As seen in the polarization diagram in Fig. 2.5, the values of $i_{o,a}$ and $i_{o,c}$ have been shown to be the same, which is not true. We can get away with this approximation primarily because the current densities at which electrolytic cells are operated are much greater than either $i_{o,a}$ or $i_{o,c}$.[11]

The polarization diagram gives a wealth of information such as E_{cell}, η_a^a, and $\left|\eta_a^C\right|$, V_a, and V_c. However, it **does not** contain information on the IR drop in the electrolyte. It is an excellent aid in understanding the kinetics of electrochemical reactions, some examples of which are given below.

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[11] However, an interesting manifestation of the superimposition of $i_{o,a}$ and $i_{o,c}$ in the polarization diagram will be discussed later in this chapter.

2.3.1 Copper electrowinning

Consider an electrolytic cell with plane-parallel electrodes of area "A". Let us assume a current $I_1 = i_1A$ is passing through the cell. With the help of the polarization diagram, calculate (i) $|E_{cell}|$, (ii) η_a^a, and $|\eta_a^c|$, and (iii) V_{cell}?

Draw a vertical line passing through i_1 in Fig. 2.5. This vertical line intersects the oxygen evolution curve at V_{a1} and the copper deposition curve at V_{c1}:

(i) The intersection of the polarization curves with the Y axis gives the value of E for the respective half-cell reactions.

$|E_{cell}|$ = reduction potential of cathodic reaction – reduction potential of anodic reaction
= $|E\ (Cu^{2+}/Cu) - E\ (O_2/H_2O)| = |E_c - E_a|$
= O_1P_1

(ii) The definition of overpotential is given in equation 2.17:

$$\eta_a^a = \Delta\phi_a - \Delta\phi_{a,e} = V_{a1} - E_a = O_1L_1 \tag{2.28}$$

$$\eta_a^c = \Delta\phi_c - \Delta\phi_{c,e} = V_{c1} - E_c = -P_1M_1 \quad (\textit{remember } \eta_a^c \textit{ is negative}) \tag{2.29}$$

$$|\eta_a^C| = P_1M_1 \tag{2.30}$$

$$V_{cell} = |E_{cell}| + \eta_a^a + \eta_c^a + |\eta_a^c| + |\eta_{ca}^c| + IR_{elec} \tag{2.31}$$

Let us assume that the concentration overpotential is negligible at both the electrodes. Therefore,

$$V_{cell} = |E_{cell}| + \eta_a^a + |\eta_a^c| + IR_{elec}$$

$$= O1P1 + O1L1 + P1M1 + IR_{elec}$$
$$= LM + IR_{elec}$$
$$= V_{a1} - V_{c1} + IR_{elec} \tag{2.32}$$

If the operating current increases from I_1 (i_1A) to I_2 (i_2A), we see that $V_{cell} - IR_{elec}$ increases from L_1M_1 to L_2 M_2. ***Equation 2.32 also suggests that, for the same ACD and electrolyte composition, as V_{cell} is increased, V_{a1} increases and V_{c1} decreases.***

In other words, if you increase the cell current, I (or, for that matter V_{cell}):

- η_a^a becomes more positive $\Rightarrow$ V_a becomes more positive
- η_a^C becomes more negative $\Rightarrow$ V_c becomes more negative

Please note that V_a and V_c do not increase in the same proportion. If the slope of the anodic polarization curve is higher, the percentage increase in V_a will be more than in V_c, the reason for which will be discussed in the section on polarization.

This example referred to the operation of the electrowinning cell in the galvanostatic (constant current) mode, which is usually the favoured mode of operation.

FFT: The problem of determining cell current and overpotentials when the cell is operated in the potentiostatic (constant potential) mode with a specified V_{cell} and R_{elec} is left as an exercise. Hint: Guess current density and iterate.

Role of R_{elec}: In the potentiostatic mode, R_{elec} reduces the magnitude of current and hence the kinetics of the half-cell reactions. In galvanostatic operation, R_{elec} increases the value of V_{cell}.

2.3.2: Copper electrowinning with copper anode

In copper electrowinning, a Pb-based anode is used and oxygen evolution is the only anodic reaction. Now let us assume that electrowinning is being carried out in a cell, with conditions similar to those in example 1, except that the Pb anode has been replaced with a copper anode. Will oxygen evolution still be the only anodic reaction?

To answer the above question, we will first consider all possible anodic reactions. Then we will use the polarization diagram to identify predominant half-cell reaction. The possible anodic reactions with a copper anode are (see Fig. 2.6):

$$Cu = Cu^{2+} + 2e$$
$$2H_2O = 4H^+ + O_2 + 4e$$

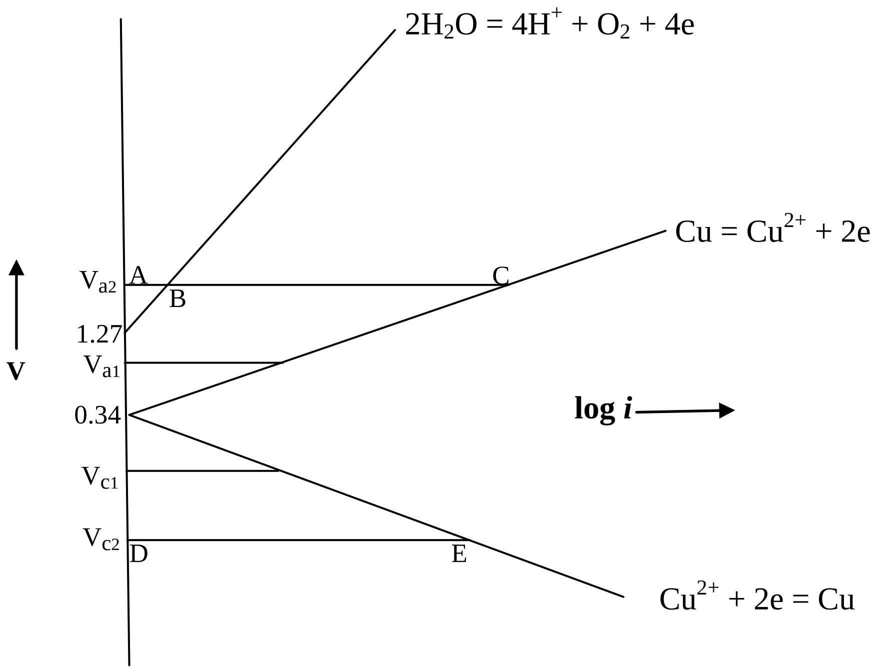

Fig. 2.6. Polarization diagram for the aqueous electrowinning of copper with a copper anode.

Assume that the cell is being operated in the potentiostatic mode. When there is no current passing through the cell, $E_a = E_c = 0.34$ V, that is $V_{cell} = 0$. As V_{cell} is increased from 0 V:

- V_a will start increasing from 0.34 V to more positive values such as V_{a1}, V_{a2} and so on.
- V_c will start decreasing from 0.34 V to less positive values such as V_{c1}, V_{c2} and so on.

Now consider the case where the magnitude of V_{cell}, say V_{cell1}, results in $V_a = V_{a1}$ and $V_c = V_{c1}$. If we draw two horizontal lines at these voltages, as shown in Fig. 2.6, we see that they intersect the polarization curves corresponding to the $Cu = Cu^{2+} + 2e$ and $Cu^{2+} + 2e = Cu$ half cell reactions. This means that the anodic and cathodic reactions correspond only to the dissolution and deposition of copper.

When we increase V_{cell} from V_{cell1} to V_{cell2}, V_a increases from V_{a1} to V_{a2} and V_c decreases from V_{c1} to V_{c2}. Now the horizontal line at V_{c2} intersects only the $Cu^{2+} + 2e = Cu$ polarization curve implying that copper deposition is the only cathodic reaction. However, the horizontal line at V_{a2} will intersect both the oxygen evolution and copper deposition curves meaning that two half cell reactions, namely, (i) $2H_2O = 4H^+ + O_2 + 4e$ and (ii) $Cu = Cu^{2+} + 2e$ are occurring at the anode.

Fig. 2.6 also shows that the oxygen evolution reaction will only take place when $V_a > 1.27$ V. However, it is clear that even at $V_a > 1.27$ V, for example V_{a2}, the copper dissolution reaction would be the predominant anodic reaction because it corresponds to a much greater value of i ($i_{Cu^{2+}}$ = AC) compared to i for the oxygen evolution reaction (i_{O_2}= AB), that is $i_{Cu^{2+}} \gg i_{O_2}$

Two points should be noted from Fig. 2.6 at V_{a2} and V_{c2} :

- The anodic current, $i_a = i_{O_2} + i_{Cu^{2+}}$ = AB + AC.
- Current efficiency of copper dissolution at the anode, $CE_{Cu}(\%) = \frac{i_{Cu^{2+}}}{i_{O_2} + i_{Cu^{2+}}}$ x 100.
- The cathodic current, i_c = DE
- In all electrolytic processes, because of continuity considerations, $i_a A_a = i_c A_c$.

Another interesting observation is that the polarization curve corresponding to oxygen evolution is **steeper** than the curve corresponding to the dissolution of copper, the reason for which will be explained in the section on polarization.

2.4 Polarization

A brief idea of polarization was given earlier. We will now visualize and formally define polarization with the help of the polarization diagram.

2.4.1 Physical picture

A half-cell reaction is polarized if its potential (V) departs increasingly from equilibrium with increasing *i*. Or, in other words, higher the slope of the polarization curve, greater the extent of polarization. That is, more energy is required for this reaction to occur.

Fig. 2.7 shows that for the H_2 evolution reaction, Pt is an ideal non-polarizable electrode, while Hg is virtually an ideal polarizable electrode.

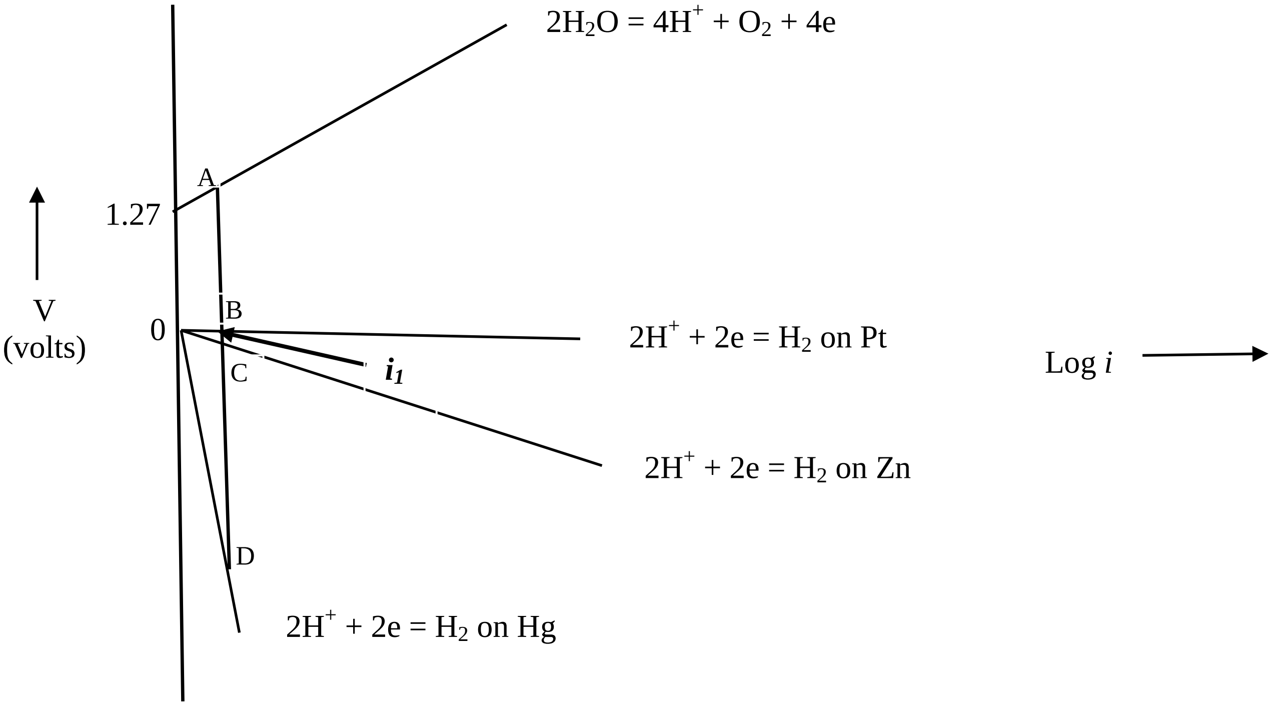

Fig. 2.7 Polarization curves for the hydrogen evolution reaction as a function of cathode material.

Let us now assume that IR_{elec} and concentration gradient can be neglected such that

$$V_{cell} = |E_{cell}| + \eta_a^a + |\eta_a^c| \tag{2.33}$$

To understand the physical meaning of polarization, consider three cells where electrolysis of dilute acidified water is being carried out. Oxygen evolution and hydrogen evolution reactions are the respective anodic and cathodic half-cell reactions. These cells are designated as 1, 2, and 3, each having a Pb anode. Cells 1, 2, and 3 have Pt, Zn and Hg cathodes respectively. All the three cells have the same (i) anode and cathode cross-sectional areas, A, (ii) anode-to-cathode distance (ACD) and (ii) electrolyte composition.

Assume that the same current I_1 (i_1 x A) passes through each of the three cells, 1, 2, and 3. V_{cell} for the three cells can now be read from Fig. 6:

$$\text{Cell 1: } V_{cell} = AB; \qquad \text{Cell 2: } V_{cell} = AC; \qquad \text{Cell 3: } V_{cell} = AD \qquad (2.34)$$

Equation 2.34 tells us that for the same current flowing through the three identical cells, the lowest voltage, and hence power (= V_{cell} x I_1) is required for cell 1 (with a Pt cathode) and highest for cell 3 (with the Hg cathode). This difference is primarily due to the kinetics of the hydrogen evolution reaction, which is a function of the cathode material. This means that the kinetics of the hydrogen evolution reaction is fastest with a platinum cathode. Or in other words, it is "easy" for the hydrogen evolution reaction to occur with a platinum cathode and very difficult for it to occur with a mercury cathode. It is also evident from Fig. 2.7 and equation 2.34 that higher polarizability is manifested in terms of larger magnitudes of overpotentials.

The previous paragraph suggests that polarizable electrodes are undesirable since they increase the power and hence energy consumption of a cell. ***Remember energy is money!!***

Polarization also has a positive effect. For example, in the electrowinning of Zn, a polarizable cathode can be used to minimize the hydrogen evolution reaction, which is thermodynamically favoured to the metal deposition reaction.

FFT: What will the product at the cathode if Zn electrowinning is carried out with a (i) Pt cathode, or with (ii) Hg cathode?

2.4.2 Polarization curves for gas evolution reactions

Polarization curves for gas evolution curves are "steeper" than metal deposition reactions, as pointed out before. That is, gas evolution reactions have higher (absolute) overpotentials than metal deposition reactions. This is due to the fact that the gas evolution reaction such as the H_2 evolution reaction is complex and occurs in several steps:

- Adsorption of H atom on the cathode surface: $H^+ + e = \rightarrow H_{ads}$
- Combination of adjoining adsorbed atoms to form H_2: $H_{ads} + H_{ads} = H_2$

Since adsorption of gas atoms is a surface dependent phenomena, the activation overpotential of gas evolution reactions will also depend on the electrode material.

2.4.3 Slope of the polarization curve and exchange current density

We have seen that polarization can be related to the magnitude of the slope of the polarization curve. Table 2.1 suggests that the exchange current density i_0 is inversely related to polarizability. That is, higher i_0 implies lower polarizability and vice-versa. Unfortunately, Tafel equation, which is the basis for the polarization diagram gives a completely different picture as shown in the following paragraph. The re-arranged form of Tafel equation for the cathodic reaction is shown below:

$$\eta_a^c = \frac{2.303RT}{\beta nF}(\log i - \log i_0) \qquad (2.35)$$

Equation 2.35 states that the slope of the polarization curve for a given half-cell reaction is a function of β and not i_0, as stated in the previous paragraph. In fact, equation 2.35 states that i_0 is related to the y-intercept of the polarization curve. What is then the reason for this glaring contradiction?

Let us redraw the polarization curve such that the $2H^+ + 2e = H_2$ reactions on Pt and Hg cathodes are not superimposed (see Fig. 2.8). Here the two polarization curves intersect the current axis at their respective exchange current densities, i_o. The slope of the two polarization curves is a function of β

(see equation 33), which does not change significantly with the cathode type. Thus the slopes of the two polarization curves in Fig. 2.8 must be approximately equal.

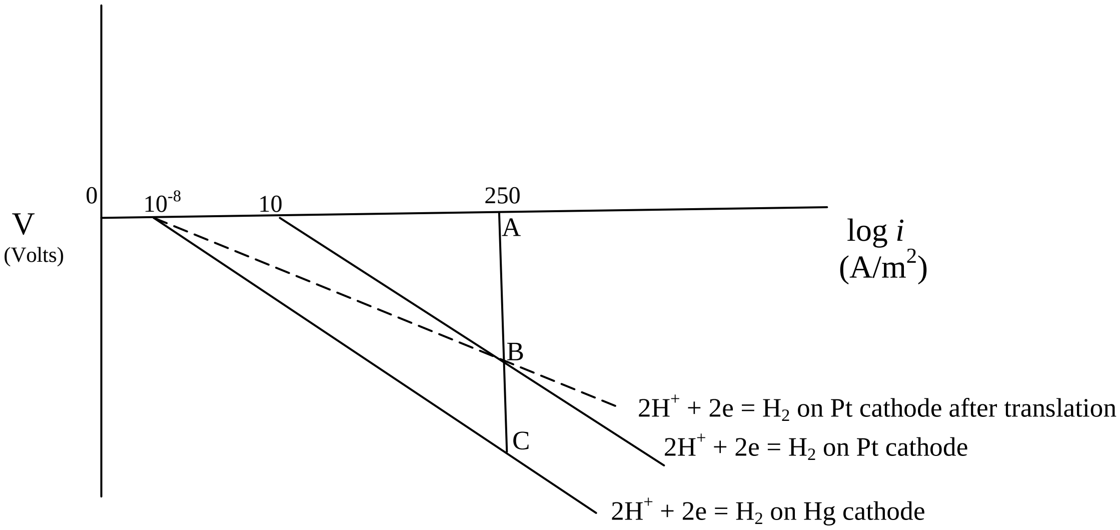

Fig. 2.8. Redrawing the polarization curves for H_2 evolution where the exchange current densities are not superimposed.

Calculate η_a^c for H_2 evolution at the two cathodes when the electrolytic cell is being operated at i = 250 A/m^2:

H_2 on Pt: $\eta_{a,Pt}^c$ = -AB
H_2 on Hg: $\eta_{a,Hg}^c$ = -AC

Translate the Pt cathode curve to the left until its x-intercept changes from 10 A/m^2 to 10^{-8} A/m^2. To maintain, the same overpotential of AB at i = 250 A/m^2, the slope of the polarization curve for the H_2 evolution reaction on Pt will decrease, as shown by the dashed line in Fig. 2.8. Hence the relation between polarizability, or the slope of the polarization curve, and i_o primarily results from the superimposition of i_o for different cathodes on one point. ***In effect, the superimposition of i_o changes the y-intercept role of i_o, as shown in equation 2.35, to that of the slope in the polarization diagram.***

2.5 Example problems

Example 2-1

Overpotential measurements at 25°C for copper dissolution in a well-stirred electrolyte yielded the following results:

i (mA/cm^2)	12	24	48	97	200	400	600	2000	20000
η_a^a (mV)	1.5	3.0	6.0	9.0	18	30	35	60	104

Determine i_o and β. η_a^a is the activation overpotential at the anode. Assume E(Cu^{2+}/Cu) = 0.34 V.

From the above data it is clear that neither the low overvoltage nor the high overvoltage approximation can be applied separately to the entire data set to determine i_o and β. Using the generalized of Butler-Volmer equation (equation 2.19) for determining i_o and β is complicated. Hence the following strategy will be adopted: (i) calculate i_o from the low overvoltage approximation, (ii) calculate β from the high overvoltage approximation. To check the accuracy of i_o and β, i will be calculated from equation 2.19 and then compared with the experimental values shown in the above table.

Remember the conventions:

- Cathodic current is “+“.
- Anodic current is “-”.
- Overpotential at the cathode is “-“.
- Overpotential at the anode is “+“.
- Current density units should be converted to A/m^2.
- Overpotential units should be converted to V.

Calculation of i_o

The reaction is $Cu = Cu^{2+} + 2e$.
For $\eta_a^a < 10$ mV

$$\eta_a^a = \frac{RTi}{nFi_o} \tag{e2-1.1}$$

Here n =2, T = 298 K, F = 96500 C/mole, R = 8.31 J/(mole K)

Plotting the first four data points as η vs i (use MS-Excel), we get a straight line with

$$\text{Slope} = \frac{RT}{nFi_o} = 10^{-4}$$

$$i_o = 128 \text{ A/m}^2 \tag{e2-1.2}$$

Calculation of β

Use the high overpotential data to calculate β: $i = 20000$ A/m^2, $\eta = 104$ mV = 0.104 V.

$$\beta = 1 - ln\left(\frac{i}{i_o}\right)\frac{1}{77\eta} = 1 - ln\left(\frac{20000}{128}\right)\frac{1}{77 \times 0.104} = 0.37 \tag{e2-1.3}$$

Substituting i_o and β, from e2-1.2 and e2-1.3 in the generalized Butler-Volmer equation, and compare the calculated and measured current densities, as shown below:

η_a^a (mV)	1.5	3.0	6.0	9.0	18	30	35	60	104
$i_{measured}$ (mA/cm^2)	12	24	48	97	200	400	600	2000	20000
$i_{calculated}$ (mA/cm^2)	15.2	31	64	101	233	501	662	2360	20180

Since the calculated and measured values of i can be as high as 30%, it means the calculated values of i_o and β was not very accurate. Can you suggest a method to extract more accurate values of i_o and β?

Example 2-2

Zinc is being deposited from a 1M $ZnCl_2$ electrolyte whose pH is 3. The electrolytic cell consists of a pair of planar electrodes. The submerged area of each electrode is 1 m^2, the anode-cathode distance (ACD) is 0.02 m, and the solution conductivity (σ) is 4 Ω^{-1} m^{-1}. At 25^{o}C both zinc deposition and hydrogen evolution are possible. Assume that the reactions follow Tafel behaviour. For the zinc reaction $\beta_{Zn} = 0.5$ and $i_{o,Zn} = 10^{-3}$ A/m^2. For hydrogen $\beta_{H_2} = 0.5$ and $i_{o,H_2} = 10^{-5}$ A/m^2. The voltage at the cathode with respect to the SCE (V_c) is – 1.2 V. Ignore activation overpotential at the anode concentration overpotential.

a) Calculate the rate of Zn deposition and V_{cell} assuming H_2 evolution is suppressed. Neglect activation overpotential at the anode.

Zn deposition rate

The rate of Zn deposition is proportional to the current density at the cathode, which is given by:

$$i_c = i_{o,Zn} \exp\left(\frac{-\beta_{Zn} n_{Zn} F \eta_{a,Zn}^c}{RT}\right) \tag{e2-2.1}$$

(Please note that the negative since on the RHS of e2-2.1 has been omitted since we are only interested in the magnitude of i_c.)

As a matter of practice, all our voltages will be described with respect to the SHE.

$$V_c\text{ (SHE)} = V_c\text{ (SCE)} + E_{SCE/SHE} = -1.2 + 0.242 = -0.96\text{ V} \qquad \text{(e2-2.2)}$$

$$\eta^c_{a,Zn} = V_c - E_{Zn^{2+}/Zn} = -0.96 - (-0.74) = -0.22\text{ V} \qquad \text{(e2-2.3)}$$

$$\beta_{Zn} = 0.5,\ \ i_{o,Zn} = 10^{-3}\text{ A/m}^2,\ n_{Zn} = 2 \qquad \text{(e2-2.4)}$$

(Please be careful with the sign associated with potentials, otherwise the answer will be way off).

Substituting values from e2-2.2 and e2-2.3 in e2-2.1, we get:

$$i_c = 10^{-3}\exp\left(-\frac{0.5\times 2\times 96500\times(-0.22)}{8.31\times 298}\right) = 5.3\text{ A/m}^2 \qquad \text{(e2-2.5)}$$

Therefore, current flowing through the cell, $I = i_c A_c = 5.3$ A

From Faraday's law, rate of Zn deposition = $\frac{64\times 5.3}{2\times 96500}$ = 0.0017g/s = 6.32 g/h.

e2-2.5 shows that more negative the value of activation overpotential, greater will be cathodic current density, and hence the cell current.

V_{cell}

$$V_{cell} = |E_{cell}| + \eta^a_a + |\eta^c_{a,Zn}| + IR_{el} \qquad \text{(e2-2.6)}$$

Reactions: C: $Zn^{2+} + 2e = Zn$ $\qquad E^{o'}_c = E^o(Zn^{2+}/Zn) = -0.74\text{ V}$

A: $2H_2O = O_2 + 4H^+ + 4e$ $\qquad E^{o'}_a = -E^o(H_2O/O_2) = -1.23\text{ V}$

$$E_{cell} = E^0_{cell} = E^{o'}_a + E^{o'}_c = -1.97\text{ V} \qquad \text{(e2-2.7)}$$

Given: $\eta^a_a = 0$ and $\eta^c_{a,Zn} = -0.22$ V

$$R_{el} \approx \frac{L}{\sigma A} = \frac{0.02}{4*1} = 0.005\ \Omega \qquad \text{(e2-2.8)}$$

e2-2.8 is only an approximation, as will be shown in the chapter on current distribution.

Hence, $\qquad V_{cell} = |-1.97| + 0 + |-0.22| + 5.3*0.005 = 2.21\text{ V}$ $\qquad$ (e2-2.9)

b) Assuming both Zn deposition and H_2 evolution reactions are occurring at the cathode, calculate the zinc deposition rate, current efficiency for zinc deposition, and V_{cell}.

When both zinc deposition and hydrogen evolution occur simultaneously at the cathode, that current at the cathode is used for both the reactions, that is,

$$i_c = i_{c,Zn} + i_{c,H_2} \tag{e2-2.10}$$

It is important to note that both the reactions will “feel” the same V_c, whose value remains unchanged at -0.96 V (see equation e2-2.2). Thus, the value of $i_{c,Zn}$ will remain the same, as in equation e2-2.5, that is, $i_{c,Zn}$ = 5.3 A/m^2. Hence the zinc deposition rate is still 6.32 g/h, as in part (a).

Current efficiency for zinc deposition (CE_{Zn})

$$CE_{Zn} = \frac{i_{c,Zn}}{i_{c,Zn} + i_{c,H_2}} \times 100 \tag{e2-2.11}$$

The expression for calculating i_{c,H_2} is given below:

$$i_{c,H_2} = i_{o,H_2} \exp\left(\frac{-\beta_{H_2} n_{H_2} F \eta^c_{a,H_2}}{RT}\right) \tag{e2-2.12}$$

$$\eta^c_{a,H_2} = V_c - E_{H^+/H_2} \tag{e2-2.13}$$

For the hydrogen evolution reaction, $H^+ + e = 0.5H_2$,

$$E_{H^+/H_2} = E^o_{H^+/H_2} - 0.059 \log\frac{P^{0.5}_{H_2}}{a_{H^+}} = -0.059\ \text{pH} = -0.059*3 = -0.18\ \text{V} \tag{e2-2.14}$$

$$\eta^c_{a,H_2} = V_c - E_{H^+/H_2} = -0.96 - (-0.18) = -0.78\ V \tag{e2-2.15}$$

(Reminder: E_{H^+/H_2} has to be used with actual sign)

$$\beta_{H_2} = 0.5,\ \ i_{o,H_2} = 10^{-5}\ \text{A/m}^2\text{, and } n_{H_2} = 1 \tag{e2-2.16}$$

$$i_{c,H_2} = 10^{-5} \exp\left[-\frac{0.5 \times 1 \times 96500 \times (-0.78)}{8.3 \times 298}\right] = 39.8\ \text{A/m}^2 \tag{e2-2.17}$$

$$i_c = i_{c,Zn} + i_{c,H_2} = 5.3 + 39.8 = 45.1\ \text{A/m}^2 \tag{e2-2.18}$$

$$CE_{Zn} = \frac{i_{c,Zn}}{i_{c,Zn} + i_{c,H_2}} \times 100 = \frac{5.3}{45.1} \times 100 = 11.7\% \tag{e2-2.19}$$

Caution: Current efficiency (*CE*) is always defined with respect to the reaction of interest, which is the deposition of Zn. Hence in Zn electrowinning, we never talk of current efficiency of H_2 evolution even though it occurs simultaneously.

V_{cell}

$$V_{cell} = |E_{cell}| + \eta^a_a + |\eta^c_a| + IR_{el} \tag{e2-2.20}$$

For calculating V_{cell} when there is more than one reaction occurring at the cathode, the ***E_{cell}* and cathodic overpotential terms in e2-2.20 should either correspond to the zinc deposition reaction or the hydrogen evolution reaction**. Therefore,

$$V_{cell} = |E_{cell}|_{Zn} + \eta_a^a + |\eta_{a,Zn}^c| + IR_{el} \qquad \text{(e2-2.21)}$$

$$= |E_{cell}|_{H_2} + \eta_a^a + |\eta_{a,H_2}^c| + IR_{el} \qquad \text{(e2-2.22)}$$

Equality of e2-2.21 and e2-2.22 can also be checked by drawing a polarization diagram. Henceforth for all problems related to zinc electrowinning $\boldsymbol{|E_{cell}| = |E_{cell}|_{Zn}}$

We will use e2-2.21 for calculating V_{cell}. Since activation overpotential for the oxygen evolution reaction at the anode is negligible, $\eta_a^a = 0$. From e2-2.3, $\eta_{a,Zn}^c = -0.22V$. I = i_c x A_c = 45.1 A.

Therefore, $\boldsymbol{V_{cell}} = |-1.97| + 0 + |-0.22| + 45.1 \times 0.005 = \mathbf{2.41\ V}$

c) What is the effect of pH on current efficiency for zinc deposition?

From e2-2.11, it is clear that pH affects CE_{Zn} through $i_{c,Zn}$ or i_{c,H_2}. Because H^+ is associated only with the hydrogen evolution reaction, CE_{Zn} is inversely related to i_{c,H_2}. e2-2.12 - e2-2.14 show that CE_{Zn} is related to pH through η_{a,H_2}^c and E_{H^+/H_2}. e2-2.14 shows that increase in pH makes E_{H^+/H_2} more negative and hence η_{a,H_2}^c less negative (see e2-2.13). e2-2.12 shows that less negative values of η_{a,H_2}^c reduces i_{c,H_2}. Consequently, an increase in pH increases CE_{Zn}.

Example 2-3

Now let us do a problem that is more frequently encountered in real-life. What would be the Zn deposition and O_2 evolution rates when a potential of 4.0 V is applied between the anode and the cathode. Assume the CE of Zn deposition is 100%. Use the cell configuration, electrolyte composition and kinetic data for Zn deposition from Example 2-2. For the O_2 evolution reaction, $\beta_{O_2} = 0.5$ and $i_{o,O_2} = 2.6 \times 10^{-7}$ A/m^2.

Since there is only one half-cell reaction at the anode and the cathode, solution of this problem requires the calculation of cell current, which, in turn, is related to the electrode current density:

$$I = i_a A_a = i_c A_c \qquad \text{(e2-3.1)}$$

It is stated that[12] $A_a = A_c$. Therefore, e2-3.1 reduces to

$$I = i_a = i_c \qquad \text{(e2-3.2)}$$

I can be obtained from the voltage balance equation.

$$V_{cell} = |E_{cell}| + \eta_{a,O_2}^a + |\eta_{a,Zn}^c| + IR_{el} \qquad \text{(e2-3.3)}$$

Given: $V_{cell} = 4.0$ V, $R_{el} = 0.005\ \Omega$, $|E_{cell}| = 1.97$ V

To obtain I from e2-3.3, we need to express η_{a,O_2}^a and $\eta_{a,Zn}^c$ in terms of I.

---

[12] In reality, because of current distribution considerations, the cathode area is normally larger than anode area in electrowinning.

Now,
$$i_a = I = i_{o,O_2} \exp\left(\frac{(1-\beta_{O_2}) n_{O_2} F \eta^a_{a,O_2}}{RT} \right) \tag{e2-3.4}$$

Remember that we have ignored the –ve sign on the RHS of the above equation.

$$\eta^a_{a,O_2} = \ln\left(\frac{I}{i_{o,O_2}} \right) \frac{RT}{(1-\beta) n_{O_2} F} = \ln\left(10^9 I\right) \frac{8.3 \times 298}{0.5 \times 1 \times 96500}$$

$$\eta^a_{a,O_2} = 0.051 \ln\left(3.85 \times 10^6 I\right) \tag{e2-3.5}$$

Similarly,

$$i_c = I = i_{o,Zn} \exp\left(\frac{-\beta_{Zn} n_{Zn} F \eta^c_{a,Zn}}{RT} \right) \tag{e2-3.6}$$

$$\eta^c_{a,Zn} = -\ln\left(\frac{I}{i_{o,Zn}} \right) \frac{RT}{\beta n_{Zn} F} = -0.026 \ln\left(10^3 I\right)$$

$$\eta^c_{a,Zn} = -0.026 \ln\left(10^3 I\right) \tag{e2-3.7}$$

Substituting e2-3.6 and e2-3.7 into e2-3.3 – 4.4 in 4.1, we get

$$4.0 = 1.97 + 0.051 \ln\left(3.85 \times 10^6 I\right) + 0.026 \ln\left(10^3 I\right) + 0.05 I \tag{e2-3.8}$$

or, I = 138 A

∴ **rate of Zn deposition** = $\frac{64 \times 138}{2 \times 96500}$ = 0.045 g/s = **0.162 kg/h**

To determine rate of oxygen evolution, consider the anodic half-cell reaction:

$$2H_2O = O_2 + 4H^+ + 4e \tag{e2-3.9}$$

From e2-3.9, we arrive at the following conclusion:

4 x 96500 C evolves 0.0224 m^3 of O_2 at STP

or, a cell current of 138 A liberates $\frac{0.0224 \times 138}{4 \times 96500}$ = 8 x 10^{-6} m^3/s of O_2.

Calculating the activation and resistance overpotentials, we get

$$\eta^a_{a,O_2} = 1\text{ V}; \quad \eta^c_{a,Zn} = -0.31\text{ V}, \quad IR_{el} = 0.69\text{ V} \tag{e2-3.10}$$

E2-3.10 suggests that the magnitude of the activation overpotential of a gas evolution reaction is more than the metal deposition reaction. We also see that resistance overpotential can indeed be significant. Here it is about 35% of the total overpotentials; which can be reduced by (i) increasing the electrolyte conductivity by adding a supporting electrolyte such as H_2SO_4 and (ii) decreasing the ACD. As usual, there is always a limit to increasing electrolyte conductivity and decreasing ACD.

What happens to the cell current if the oxygen evolution reaction becomes ideally non-polarizable, i.e., $\eta^a_{a,O_2} = 0$ V?

e2-3.8 now becomes

$$4.0 = 1.97 + 0.026\ln\left(10^3 I\right) + 0.05I \qquad \text{(e2-3.11)}$$

$$\mathrm{I} = 340\ \mathrm{A}$$

Thus we see that when the oxygen evolution reaction is ideally non-polarizable, the cell current increases from 138 A to 340 A. Thus polarization, as stated before, can be viewed as an additional "resistance."

Example 2-4

Let us now re-do Example 2-3 by assuming that current efficiency of Zn deposition is not 100%. That is, all three reactions, namely H_2 evolution and Zn deposition at the cathode and O_2 evolution at the anode are polarized.

Again, we have to determine cell current, I.

The voltage balance now becomes:

$$V_{cell} = \left|E_{cell}\right| + \eta^a_{a,O_2} + \left|\eta^c_{a,Zn}\right| + IR_{el} \qquad \text{(e2-4.1)}$$

Given: $V_{cell} = 4.0$ V, $R_{el} = 0.005\ \Omega$, $\left|E_{cell}\right| = 1.97$ V, $i_a = i_c = I$ (e2-4.2)

Because two half-cell reactions are occurring at the cathode:

$$i_c = i_{c,H_2} + i_{c,Zn} \qquad \text{(e2-4.3)}$$

or,

$$i_{c,Zn} = xI \qquad \text{(e2-4.4)}$$

where, x = fractional current efficiency for Zn deposition

From e2-3.5, we get,

$$\eta^a_{a,O_2} = 0.051\ln\left(3.85\times10^6 I\right) \qquad \text{(e2-4.5)}$$

Now,

$$i_{c,Zn} = xI = i_{o,Zn}\exp\left(\frac{-\beta_{Zn}n_{Zn}F\eta^c_{a,Zn}}{RT}\right) \qquad \text{(e2-4.6)}$$

$\therefore$

$$\eta^c_{a,Zn} = -0.026\ln\left(10^3 xI\right) \qquad \text{(e2-4.7)}$$

Substituting equations e2-4.5 and e2-4.7 in e2-4.1, we get

$$4.0 = 1.97 + 0.051\ \ln(3.85 \text{ x } 10^6 I) + 0.026\ \ln(10^3 xI) + 0.005I$$

or, $$0.051 \ln(I) + 0.026 \ln(xI) + 0.05I = 1.08 \qquad \text{(e2-4.8)}$$

e2-4.8 has two unknowns *x* and *I,* which can be solved for iteratively with the following algorithm:

a) Guess a value for $x = x_i$. The subscript "*i*" refers to iteration number.

b) Calculate I_i from e2-4.8.

c) Calculate $\eta^c_{a,Zn}$ from e2-4.7.

d) Calculate $V_c = E_{Zn^{2+}/Zn} + \eta^c_{a,Zn}$.

e) Calculate $\eta^c_{a,H_2} = V_c - E_{H^+/H_2}$.

f) Calculate $i_{c,H_2} = i_{o,H_2} \exp\left(\frac{-\beta_{H_2} n_{H_2} F \eta^c_{a,H_2}}{RT}\right)$.

g) Calculate current efficiency, $x_{i+1} = 1 - \frac{i_{c,H_2}}{I}$.

h) If $x_{i+1} = x_i$, then the guessed value of *x* is correct. Otherwise go to step (a) with $x = x_{i+1}$ and iterate until convergence.

Let us start the iteration.

a) Guess $x_1 = 0.2$.
b) From equation 4.7, we get $I_1 = 140$ A.
c) From equation 4.6, $\eta^c_{a,Zn} = -0.27$ V.
d) $V_c = -0.74 + (-0.27) = -1.01$ V.
e) $\eta^c_{a,H_2} = -1.01 - (-0.18) = -0.83$ V.
f) $i_{c,H_2} = 107$ A/m^2; $I_{c,H_2} = 107A$.
g) $x_2 = 0.23$.

Since $x_2 \approx x_1$, our initial guess of x =0.2 and hence the values of currents and overpotentials listed during the first round of iteration are reasonably accurate. Now you can go ahead an calculate the Zn deposition and oxygen evolution rates.

Example 2-5

A zinc electrolysis cell is operating at 80% current efficiency with electrodes of area 1.0 m^2, ACD of 0.02 m, and an electrolyte with a conductivity of 4 Ω^{-1} m^{-1}. The polarization equations for the anodic and cathodic reactions are given below:

Anode (O_2 evolution reaction): $V_a = 1.44 + 0.07 \log i$

Cathode (Zn deposition) $V_c = -0.86 - 0.08 \log i_{Zn}$

Cathode (H_2 evolution) $V_c = -0.6 - 0.3 \log i_{H_2}$

a) Calculate the total current flowing through the cell.
b) Calculate the rate of oxygen evolution at the anode?
c) What is the voltage drop across the electrolyte?
d) What is the value of V_{cell}?

Given: $A_c = A_a = 1.0$ m^2, Anode-to-cathode distance= $l = 0.02$ m, $\sigma = 4\ \Omega^{-1}$ m^{-1}, $CE_{Zn} = 0.8$.

a) We know that total current,

$$I = (i_{Zn} + i_{H_2})A_c = i_{Zn} + i_{H_2} \qquad \text{(e2-5.1)}$$

Since $CE_{Zn} = 0.8$, we have,

$$i_{Zn} = 4i_{H_2} \qquad \text{(e2-5.2)}$$

Now, I cannot be determined by the procedure outlined in Example 2-4 because the kinetic parameters, namely β and i_o of the three half-cell reactions are not given. Instead we will use the concept that V_c felt by both the cathodic half-cell reactions is the same, that is,

$$-0.86 - 0.08 \log i_{Zn} = -0.6 - 0.3 \log i_{H_2} \qquad \text{(e2-5.3)}$$

Substituting e2-5.2 in e2-5.3, we finally get:

$$i_{H_2} = 25.16 \text{ A/m}^2,\ i_{H_2} = 100.64 \text{ A/m}^2, \text{ and } \boldsymbol{I = 125.8 \text{ A}}$$

b) Since current flowing through the anode equals the current flowing through the cathode, and there is only one half-cell reaction at the anode ($2H_2O = 4H^+ + O_2 + 4e$), the rate of oxygen evolution will correspond to a current of 125.8 A.

$$\therefore \text{ rate of oxygen evolution} = \frac{125.8 \times 0.0224}{4 \times 96500} = 7.3 \times 10^{-6} \text{ m}^3\text{/s at STP.}$$

c) Voltage drop across the electrolyte, $IR_{elec} = \dfrac{I.ACD}{\sigma A} = \dfrac{125.8 \times 0.02}{4 \times 1} = 0.63$ V

$$V_{cell} = |E_{cell}| + \eta^a_{a,O_2} + |\eta^c_{a,Zn}| + IR_{el} \qquad \text{(e2-5.4)}$$

Given: $E^o_{O_2/H_2O} = 1.2$ V, $E^o_{Zn^{2+}/Zn} = -0.74$ V, $E_{cell} = E^o_{cell} = -1.96$ V (e2-5.6)

$$\eta^a_{a,O_2} = V_a - E_{O_2/H_2O} = (1.44 + 0.07 \log i) - E^o_{O_2/H_2O} \qquad \text{(e2-5.7)}$$
$$= 1.44 + 0.07 \log(125.8) - (+1.2)$$
$$= 0.39 \text{ V}$$

$$\eta^c_{a,Zn} = V_{c,Zn} - E_{Zn^{2+}/Zn} = -0.86 - 0.08 \log i_{Zn} - E^o_{Zn^{2+}/Zn} \qquad \text{(e2-5.8)}$$
$$= -0.86 - 0.08 \log(100.64) - (-0.74)$$
$$= -0.28 \text{ V}$$

$$\therefore \qquad V_{cell} = 1.96 + 0.39 + 0.28 + 6.29 = 8.9 \text{ V}$$

Example 2-6

Fig. f2-6.1 shows the polarization diagram for the electrowinning of Zn. It is assumed that the cell is being operated at a constant current such that $V_c = -1.0$ V with respect to a SHE. Calculate the activation overpotential of the cathodic half-cell reactions and the current efficiency of Zn deposition.

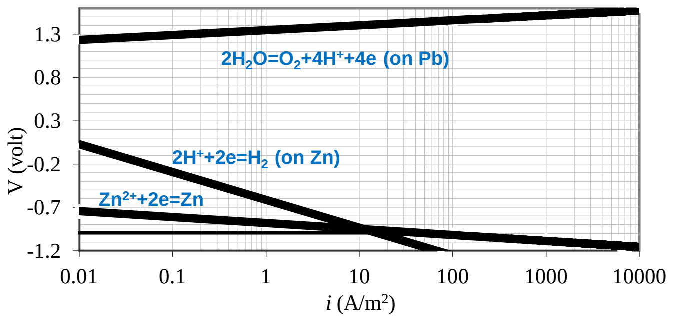

Fig. f2-6.1. Polarization diagram for zinc electrowinning.

It is seen in Fig. f2-6.1 that a horizontal line drawn at $V = V_c = -1.0$ will intersect both the zinc deposition and the hydrogen evolution curves at $i \approx 15$ A/m^2

$$\eta_a^{c,Zn} = V_c - E_{Zn^{2+}/Zn} = -1.0 - (-0.76) = -0.24\,V.$$

$$\eta_a^{c,H_2} = V_c - E_{H^+/H_2} = -1.0 - 0 = -1.0\,V.$$

From Fig. f2-6.1, we see that:

$$i_{Zn} = 15 \text{ A/m}^2\,; \qquad i_{H_2} = 15 \text{ A/m}^2$$

Current efficiency for Zn deposition = $\dfrac{i_{Zn}}{i_{H_2} + i_{Zn}}$ x 100 = 50%