NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: 409

COURSE TITLE: ELECTROCHEMISTRY

COURSE GUIDE

CHM 409

ELECTROCHEMISTRY

COURSE TEAM:

NATIONAL OPEN UNIVERSITY OF NIGERIA

National Open University of Nigeria

Headquarters

14/16 Ahmadu Bello Way

Victoria Island, Lagos

Abuja Office

5 dares Salaam Street

Off Aminu Kano Cresent

Wuse II, Abuja

Email: centralinfo@nou.edu.ng

URL: www.nou.edu.ng

Published by

National Open University of Nigeria

Printed 2013

ISBN:

CONTENTS PAGE

COURSE GUIDE

Electrochemistry is a science that studies the interaction of chemical and electrical energies. This includes the study of chemical changes caused by the passage of an electric current across a medium, as well as the production of electric energy by chemical reactions. Electrochemistry also embraces the study of electrolyte solutions and the chemical equilibria that occur in them.

Many chemical reactions require the input of energy and can be carried out in an electrochemical cell connected to an external power supply. These reactions provide information about the nature and properties of the chemical species contained in the cells, and can also be used to synthesize new chemicals. The production of sodium, chlorine and aluminium; and the electroplating and electrowinning of metals are examples of industrial electrochemical processes. Other examples are cathodic and anodic protection of metals against corrosion. Electrochemical cells that produce electric energy from chemical energy are the basis of primary and secondary (storage) batteries and fuel cells. Other electrical phenomena of interest in chemical systems include the behaviour of ionic solutions and the conduction of current through these solutions, the separation of ions by an electric field (electrophoresis), the corrosion and passivation of metals, electrical effects in biological systems (bioelectrochemistry), and the effect of light on electrochemical cells (photoelectrochemistry).

In electrochemistry, two broad areas are involved. These are electrodics and ionics. Ionics deals with ions in solution and conductivity; while electrodics deals with the production of electricity by electrochemical reactions and the production of electrochemical reactions by an applied electromotive force.

Let us examine the basic features in ionics, which involves conductivity. In electrolytes, conductivity is due to mobility of ions. When a salt is dissolved in water, the energy required is provided by hydration. The extent of hydration depends on the size and charge of the ion. A small highly charged ion such as Al^{3+} will be more hydrated than K^+. Hydrated ions of opposite charges show little tendency to attract ions in dilute solution because the high permittivity (ε) of water reduces the force between charges (i.e, F), q_1 and q_2 which can be expressed as:

$$F = \frac{q_1 q_2}{4\pi l^2 \varepsilon} \qquad 1$$

where l is the distance of separation between the charges. For water, ε = 78.54 at 298 K.
Also, association of water molecule with ions (i.e hydration sheaths), which is capable of inhibiting ionic association, can hinder conductivity. For example, at high concentration, Mg^{2+} and SO_4^{2-} associate according to the following equation:

$$Mg^{2+} + SO_4^{2-} = Mg^{2+}SO_4^{2-} \qquad 2$$

This association can hinder the conductivity of the electrolyte since ions pairs do not conduct electricity.

An electrochemical cell generally consists of two half-cells, each containing an electrode in contact with an electrolyte. The electrode is an electronic conductor (such as a metal or carbon) or a semiconductor. Current flows through the electrodes via the movement of electrons. An electrolyte is a phase in which charge is carried by ions. Normally, positive ions move towards the negative electrode (cathode) while negative ions move towards the positive electrode (anode). The movement of electrons always proceed in the opposite direction; that is, electrons move from the anode to the cathode.

The half-cells are connected by a cell separator that allows ions to move between the half-cells but prevents mixing of the electrolytes. The separator can consist of a salt bridge, or tube of aqueous solution plugged at both ends with glass wool, or it can be an ion exchange membrane or a sintered-glass disk. In some cases both half-cells use the same electrolyte, so that the electrochemical cell consists of two electrodes in contact with a single electrolyte. Electrochemical cells are usually classified as either galvanic or electrolytic. In galvanic cells, reactions occur spontaneously at the electrode–electrolyte interfaces when the two electrodes are connected by a conductor such as a metal wire. Galvanic cells convert chemical energy into electric energy and are the components of batteries, which usually contain several cells connected in series. In electrolytic cells, reactions are forced to occur at the electrode–electrolyte interfaces by way of an external source of power connected to both electrodes. Electric energy from the external source is converted to chemical energy in the form of the products of the electrode reactions.

In this course, we shall examine some fundamental aspects of ionics including mass transport, polarization, interfacial interaction, polarography and associated laws or theories. In view of this, we shall consider some basic principles underlying the behaviour of ions in solution.

COURSE DESCRIPTIONS

Electrochemistry (CHM 409) is a course which addresses the behaviour of ions in solutions. CHM 409 is structured to address the theory, principles and application of what happens around electrochemical the interface. The study of electrochemical interface is significant because most of the usefulness of electrochemistry rest on processes at the interface. In view of this, the course introduces the meaning of an electrochemical interface and examines the type of electrochemical interfaces, the electric double layer, and mass transport of materials from and through the interface, polarization at the interface, polarography and electronics in electrochemistry.

COURSE AIMS

This course is aimed to bring the student to the knowledge of fundamental aspects, theory and laws in ionics, an aspect of electrochemistry that deals with ions in solutions. Students will learn the concept of electric double layer, potential at zero charge, mass transport, polarization, overpotential, interfacial interactions and some laws including Ficks law, Butler-Volmer, Einstein, Stoke, Wagner, Ilkovic and Levish laws of electrochemistry.

COURSE OBJECTIVES

- To introduce the concept of electric double layers and their effect on electrochemical systems
- To bring the student to the understanding of the meaning of potential at zero charge and how it can be measured
- To explain the concept of polarization of electrodes and other electrochemical interfaces
- To introduce and explain the various forms of mass transport in electrochemical systems
- To introduce and explain the concept of polarography and its application in electrochemistry
- To explain the concept of electronics in electrochemistry
- To explore the theories and laws associated with all the listed concepts

WORKING THROUGH THIS COURSE

The course is structured into five models. Modules 1 to 3 consist of two units each while modules 4 and 5 consist of one unit each. It is necessary that for the student to study and understand the content of all the units in the respective modules.

COURSE MATERIALS

You will be provided with the following materials:

1. Course Guide

2. Study Units

STUDY UNITS

Module 1

Unit 1: Electrochemical interface

Unit 2: Electric double layer

Module 2

Unit 1: Polarization at interface

Unit 2: Verification of Tafel equation; Butler-Volmer equation

Module 3

Unit 1: Mass transport

Unit 2: Polarography

Module 4

Electronics in electrochemistry

Module 1 introduces the students to electrochemical interfaces and electric double layer.

Unit 1 identifies the different forms of electrochemical interfaces and discusses their structure, features and possible applications. Some notable scientists that have contributed to the development of electrical interfaces have also been acknowledged.

In **unit 2**, electric double layer is introduced as a process that is significant at the interface. Different models including Guoy-Chapman model, Stern model and Classical model have been considered.

Module 2 is also divided into two units.

Unit 1 considers polarization at electrochemical interfaces. Polarization of single and complete electrodes is considered. Different types of polarization and their implications have also been singled out and discussed. Diagrams have been presented in order to facilitate ease of understanding. Models governing concentration, activation and total polarizations have been derived and discussed. The unit is simplified by analysing some typical examples obtained from other studies.

Unit 2 attempts to verify Tafel law, which is simplified by the derivation of Butler-Volmer equation. Applications of the equation in practical fields are presented in a form that should be understandable by the student.

Module 3 consists of two one units.

Unit 1 examines mass transport. Diffusion, convection and migration are identified as the three major ways of mass transport in electrochemical interfaces. Derivation of Ficks law and its implications has been extended in order to simplify diffusion as a means of mass transport. Migration has also been singled out and discussed, and the equation connecting the three mass transport processes is presented and discussed.

Unit 2 presents the science of polarography, its principles, application and theory. The basic features of the polarogram, which is the half-wave potential has been discusses in details. Diagrams are presented to aid the students' comprehension and understanding of polarography.

Module 4 highlights electronics as a fundamental need in electrochemistry. Some circuit elements have been highlighted and practical circuit diagram in some electrochemical analysis has also been presented.

TEXTBOOKS AND REFERENCES

Textbooks referred to in the development of each unit are presented at the end of the units. However, a list of some General references is presented below:

1. Atkins, P. and De Paula, J. (2010). Atkins'Physical Chemistry.Ninth Edition.Oxford University Press. UK.
2. Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.
3. Levine, N. I. (2009). Physical Chemistry.5th Edition.Higher Education. Boston.
4. Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.
5. Onuchukwu, A. I. (2008). Electrochemical technology. Spectrum Books Limited. Nigeria.

6. Zamec, Z. (2004). Electrochemistry at the interface between two immiscible electrolyte solutions **(IUPAC Technical Report).***Pure and Applied Chemistry* 76(12); 2147–2180.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and end of course examination. The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30 % of the total course score. Each learner shall be examined in four TMAs before the end of course examination. The end of course examination shall constitute 70% of the total course score.

MAIN COURSE

CONTENTS

MODULE 2

Unit 1: Polarization at interface

1.0 Introduction

2.0 Objectives

3.0 Main content

- 3.1 Polarizable and non-polarizable interfaces
- 3.2 Polarization of a single electrode
- 3.3 Dependent of activation overpotential on current

UNIT 2: Verification of Tafel Equation: Butler-Volmer law

1.0 Introduction
2.0 Objectives
3.0 Main content
- **3.1 Derivation of Butler Volmer equation**
- **3.2 Experimental determination of current and Tafel plot**
- **3.3 Significance of Tafel plot**
- **3.4 Modelling of concentration potential**
- **3.5 Total overpotential**

4.0 Conclusion
5.0 Summary
6.0 References/Further reading

MODULE 3:

Unit 1: Mass Transport

1.0 Introduction

2.0 Objectives

3.0 Main content

- **3.1 Mass transport in electrochemical systems**
- **3.2 Transport of ions in electrolyte**
- **3.3 Rotating disc electroscope theory: Levich equation**
- **3.4 Application of Levich equation**

4.0 Conclusion

5.0 Summary

6.0 References/Further reading

MODEL 1

UNIT 1

1.0 Introduction

Electrochemistry is concerned with the study of interaction between electrical and chemical effects. This implies that chemical energy can be converted into electrical energy and vice versa. Every electrochemical system must have the electrodes (cathode and anode) and the electrolytes. It has been found that an electrochemical system is not a homogenous system, but rather a heterogeneous one. Therefore, there exist certain regions called interfaces within electrochemical systems.

An electrochemical system can also be defined as a system in which there is a difference of electric potential between two or more phases. The difference in potentials can arise in several ways but the significant ones are

i. Charge transfer between metal-solution interface
ii. Charge transfer between metal-metal interface
iii. Charge transfer between solution-solution interface

The magnitude of the potential controls the direction and the rate of charge transfer at the electrochemical interface. The study of charge transfer at the interface is significant because most advantages and applications that can be derived from electrochemical systems reside or position themselves within the interface. Therefore, this section shall examine the various electrochemical interfaces and how they are positioned or organised within an electrochemical system.

2.0 Objectives

At the end of this Unit, students should be able to:

- Introduce and explain the different types of interfaces in electrochemistry
- Explain the concept of charge transfer through interfaces
- Highlight factors that influence complex distribution of electric charge in interfaces
- Use suitable diagrams to explain metal-metal and metal–solution interfaces

3.0 MAIN CONTENT

3.1 Types of interface

There are basically two major types of electrochemical interfaces and are highlighted below:

3.1.1 Metal-solution interface: There exists a potential in a metal-solution interface. For this system, the magnitude and sign of the potential depends on temperature, pressure, nature of the solvent and the concentration of metal ions in the solution.

Example of cases where metal-solution interface potential exists is the K^+/KCl interface. For example, suppose a membrane permeable to K^+ ions but not to Cl^- ions separates an aqueous KCl solution from pure water. Diffusion of K^+ ions through the membrane will produce net charges on each phase and a potential difference between the phases. Another example is an electrochemical system consisting of a piece of Zn metal dipped into an aqueous solution of $ZnSO_4$ as shown in Fig.1.1

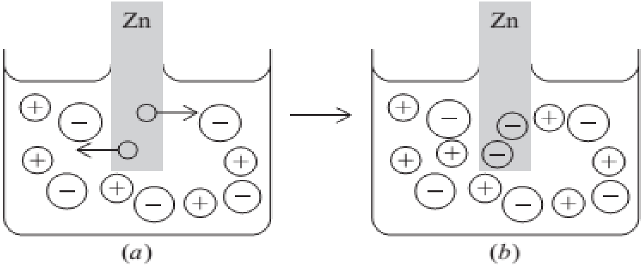

Fig. 1.1: Development of electric potential differences between $Zn_{(s)}$ and $ZnSO_{4\,(aq)}$

The zinc metal consists of ions and mobile electrons. Its ions can be transferred between the metal and the solution but its electrons cannot enter the solution. Since the zinc metal and the solution contain zinc ions, there are two ways in which the ions can migrate. These include movement of zinc ions from the metal to the solution and the migration from the solution to the zinc metal. If the $ZnSO_4$ solution is extremely dilute, then the initial rate at which Zn^{2+} ions leave the metal and enter the solution is greater than the rate at which Zn^{2+} ions enter the metal from the solution. This net loss of $Zn^{2+}$from the metal produces a negative charge (excess of electrons) on the Zn, which will slow the rate of the process at which Zn^{2+} ions migrate from the metal to the aqueous solution (equation 1.1) and increase the rate of the process in which Zn^{2+} ions migrate from the aqueous solution to the metal (equation 1.2)

$$Zn^{2+}_{(metal)} \rightarrow Zn^{2+}_{(aq)} \qquad 1.1$$

$$Zn^{2+}_{(aq)} \rightarrow Zn^{2+}_{(metal)} \qquad 1.2$$

At equilibrium, the rates of these opposing processes are equal and the Gibbs energy (*G)* of the system is a minimum. Also, at equilibrium, the Zn has a net negative charge, and a potential difference $\Delta\phi$ exists between Zn and the solution.

3.1.2 Metal-metal interface: In metals, diffusion is very slow, especially at room temperature. Consequently, metal ions do not move at ease within the phase. However, electron moves freely from one metal atom to another, such that at equilibrium, net negative and positive charges are respectively left in each of the metal atoms. A typical example is the interface that can be created when Cu and Zn metals ate joined together; net positive and negative charges would be produced on the Cu and on the Zn respectively (Fig. 1.2). The magnitude of the potential difference between the copper and zinc metals will depend on temperature.

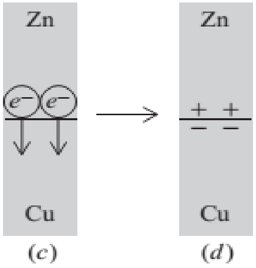

Fig. 1.2: Development of electric potential between $Zn_{(s)}$ and $Cu_{(s)}$

2.1.3 Solution-solution interface

Although solution-solution interface is not as common, it does exist between two immiscible electrolyte solutions, and is formed between two liquid solvents of low mutual miscibility, each containing an electrolyte. One of these solvents is usually water, and the other one a polar organic solvent of a moderate or high dielectric permittivity, (For example, nitrobenzene or 1, 2-dichloroethane), that can encourage partial dissociation of dissolved electrolyte(s) into ions.

Detail electrochemical study on solution-solution interface is beyond the scope of this course. However, it is significant to state that this type of interface find wider applications; including electroanalysis, phase-transfer catalysis, ion extraction, and electrocatalysis.

4.0 Conclusion

Interface is a boundary condition that cannot be eliminated or avoided in electrochemical systems. Although electrochemical interfaces can be a source of obstruction to free flow of ions or materials across the electrodes, its importance cannot be overemphasised. Therefore, the study of the chemistry of interface is significant. Therefore in Unit 2 of this module, we shall continue to examine several processes that can occur in an electrochemical interface.

5.0 Summary

The transfer of charge between two phases, α and β will produce a difference in electric potential between the phases. Let the potentials in the bulk of each of the phases be ϕ^{α} and ϕ^{β} respectively. It can be shown that $\phi^{\alpha} \neq \phi^{\beta}$. The electric potential in the bulk of a phase is called inner potential or the Galvanic potential.

The interface region between two bulk phases usually contains a complex distribution of electric charge resulting from

(*a*) charge transfer between phases,

(*b*) unequal adsorption of positive and negative ions,

(*c*) orientation of molecules with permanent dipole moments,

(*d*) distortion (polarization) of electronic charge in molecules.

Due to the above listed effects, several processes occurring at the interface must be studied in order to acquire a deeper understanding of an electrochemical system. In this section we shall consider electric double layer, polarization/over voltage and other processes.

7.0 Tutor-marked assignments

1. Highlight the different processes that can create a potential difference in an electrochemical system
2. List the three major electrochemical interfaces that you know and explain the order expected for diffusion of ions or other elementary particles in each of them

3. What factors are responsible for a complex distribution of charge within the interface region of an electrochemical system
4. In every electrochemical system, it is required that there should be an anode and a cathode. If a piece if iron metal is immersed in a solution of HCl, do you expect to have the anode and the cathode in that system? Give reasons for your answer.

References/Further reading

Atkins, P. and De Paula, J. (2010). Atkins'Physical Chemistry.Ninth Edition.Oxford University Press. UK.

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry. 5th Edition.Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

Zamec, Z. (2004). Electrochemistry at the interface between two immiscible electrolyte solutions (IUPAC Technical Report).*Pure and Applied Chemistry* 76(12);2147–2180.

UNIT 2: Electric double layer

1.0 Introduction

2.0 Objectives

3.0 Main content

  3.1 The electric double layer

  3.2 The double layer models

    3.2.1 The Stern model

    3.2.2 The Classical model

  3.3 Application of electric double layer

  3.4 Potential at zero charge

4.0 Conclusion

5.0 Summary

6.0 References/Further reading

1.0 Introduction

At any electrode immersed in an electrolyte solution, a specific interfacial region is formed. This region is called the double layer. The electrical properties of such a layer are important, since they significantly affect electrochemical measurements. If an electrical circuit used to measure the current that flows at a particular working electrode, the double layer can be viewed as a capacitor.

The electric double layer structure and its capacity depend on several parameters such as: electrode material (metals, carbons, semiconductors, electrode porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature. The composition of the double layer influences the electron transfer rate. Therefore, this section shall consider the concept of the electric double layers, their significance and applications.

2.0 Objectives

At the end of this unit, you should be able to:

- introduce the concept of electric double layer
- highlight the three major zones that exist in electrochemical systems
- state the different sections in an electric double layer
- describe the different models behind the electric double layer

- state the application of electric double layer
- explain the concept of potential at zero charge and it's significance.

3.0 Main content

3.1 The electric double layer

The application of a potential to an electrochemical cell can cause the surface of the electrode to be charged and this will lead to the formation of an electric double layer. The electrode can be charged by specific adsorption of molecules onto its surface. An electric double layer is therefore formed by the adsorption of counter-ions and desorption of co-ions at the interface relative to the concentration in the bulk. Historically, charge distribution at the interface is called electric double layer because the distribution conforms to every positive ion being surrounded by negative ions and vice versa.

In order to gain more insight into the concept of the electric double layer in an electrochemical cell, we can consider a typical electrochemical compartment to be a universe of three major subsets: (Fig. 1.3)

i. The electrode
ii. The interfacial region (extending from 0.5 to 100 nm)
iii. The bulk solution

At the electrode, Faradic electron transfer occurs at its surface. In the interfacial region, non-Faradic transfer occurs. Ionic concentration differs from that of the bulk solution because of polarization and the production of electric double layer. These changes affect the current and cell potential. In the bulk solution, mass transfer from bulk solution to electrode surface occurs. The kinetics of such transfer is governed by diffusion and convection. It follows from the above that electric double layer is an interfacial process

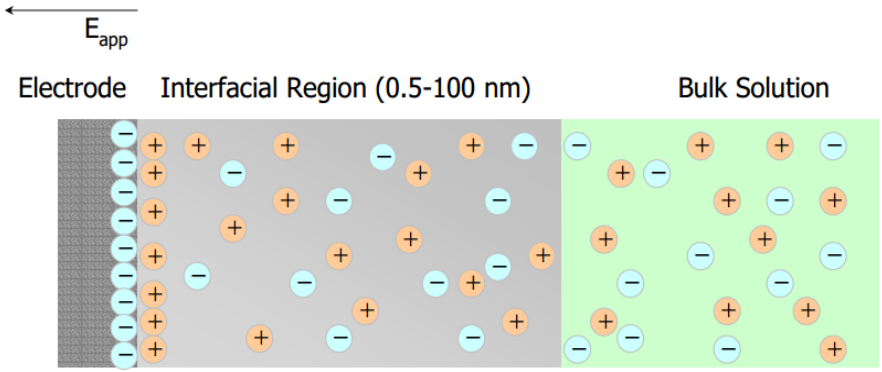

Fig. 1.3: Different zones around the electrode

A simple demonstration of the double layer process is the interface between a metal electrode and an aqueous electrolyte solution, for example, between Cu and $CuSO_4$ (*aq*). Suppose the electrode is positively charged because of a net gain of Cu^{2+} ions from the solution, the formation of double layer will ensure that the positively charged electrode is surrounded by negatively charged ions from the solution. Engel and Reid (2006) modelled the electric double layer phenomenon in terms of the parallel plate capacitor as shown in Fig. 1.4. In the Figure, the positively charged plate of the capacitor is represented by the metal electrode and the negative plate is made of negative ions that are surrounded by their solvation shell. The two types of negative ions at the interface are distinguished by the forces that hold them in this region. Specifically bound ions are those that form a bond with the surface of the electrode (example of specifically adsorbed ions are Cl^- and Br^- ions). For these ions, the water molecule in their solvation shell is not as strongly bound compared to positive ions like K^+ and Na^+. The plane that goes through the centre of the specifically adsorbed ion is called inner Helmholtz plane (IHP). The second type of ion that are found outside the electric double layer are the fully solvated ions, which are called non-specifically adsorbed ions and the plane that goes through their centre is called outer Helmholtz plane (OHP). The zone between the OHP and the bulk solution is the diffuse layer

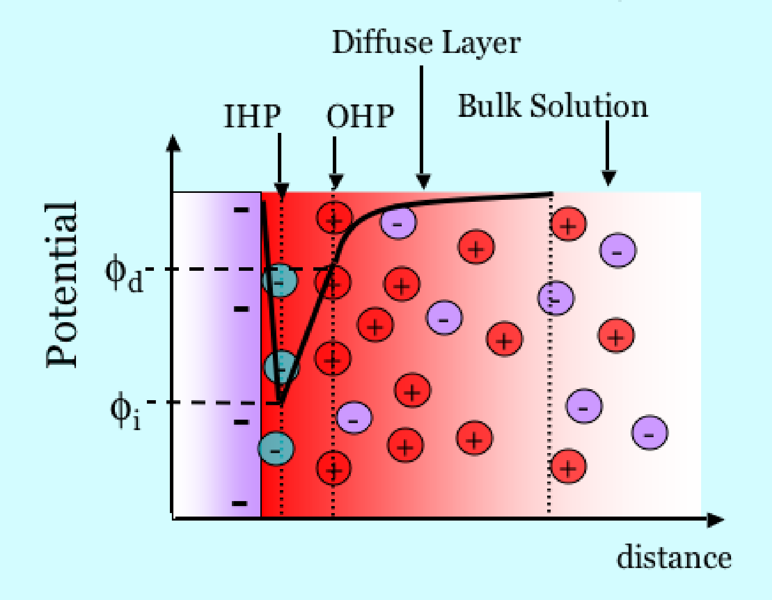

Fig. 1.4: Different sections in an electric double layer
(Source: https://www.google.com.ng/search?q=electric+double)

3.2 The double layer models

The concept of the existence of the double layer at the surface of a metal being in contact with an electrolyte appeared in 1879 (Helmholtz). That first theoretical model assumed the presence of a *compact layer* of ions in contact with the charged metal surface. The next model, of Gouy and Chapman, involved *a diffuse double layer* in which the accumulated ions, due to the Boltzmann distribution, extend to some distance from the solid surface. In further developments, Stern (1924) suggested that the electrified solid-liquid interface includes both the rigid Helmholtz layer and the diffuse one of Gouy and Chapman. Specific adsorption of ions at the metal surface was pointed out by Graham in 1947. In consecutive developments, the role of the solvent has been taken into account (Parsons 1954; Bockris 1963). It soon became clear that in dipolar solvents, such as water, the dipoles must interact with the charged metal surface. It is also worth noting here that these interactions are promoted by the high concentration of the solvent, which is usually at least several moles per litre, and, in particular, for water it is around 55.5 M. In his theory, Parsons recognized that the dielectric constant of the solvent in the compact layer of adsorbed molecules is much lower compared to the outer region and approaches the limiting Maxwell value.

3.3 Stern model

In 1924, Stern proposed that some of the excess negative ions in the solution are adsorbed on the electrode and held at a fixed distance determined by the ionic radius while thermal motion distributes the remainder of the excess negative ions diffusely in the interface region (Fig. 13.19*a*). Figure 1.5 shows the variation in the electric potential ϕ with distance from the electrode, as calculated from the Stern model. As we go from phase α to phase β, the electric potential in the interface region gradually changes from ϕ^{α} to ϕ^{β}. If z is the direction perpendicular to the α-β interface, the derivative $\delta\phi\delta z$ is non-zero in the interface region, which also implies that the electric field, $E_z = - \delta\phi\delta z$ is non-zero in the interface region. An ion or electron with charge Q that moves from the bulk phase α to the bulk phase β experiences an electric force in the interface region and has its electrical energy changed by $(\phi^{\beta} - \phi^{\alpha})Q$.

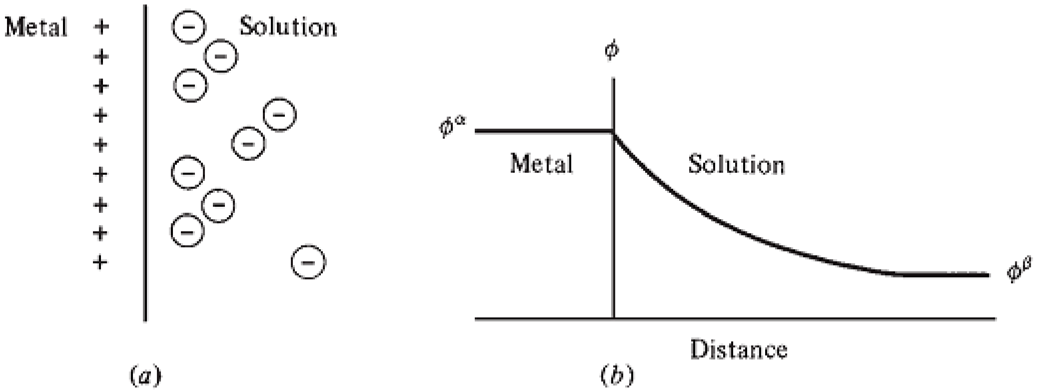

Fig. 1.5: Variation in the electric potential ϕ with distance from the electrode (according to stern model)

3.4 The classical model

A classic, simplified model of the double layer formed at the metal electrode surface is presented in Fig. 1.6. There is a layer of adsorbed water molecules on the electrode surface. Since it has been assumed that there is excess of negative charge at the metal phase, the hydrogen atoms of adsorbed water molecules are oriented towards the metal surface. However, it is not a prerequisite that all water molecules at a particular electrode potential and the corresponding excess charge have the same orientation. For excess of positive charge at the metal surface, the dipoles of water will have different orientations. A specifically adsorbed large neutral molecule is also shown in Fig. 1.6. This molecule has removed some water molecules from the surface. On the other hand, a hydrated cation present at the surface has not removed surface water, and therefore cannot be considered as specifically adsorbed. Two planes are usually associated with the double layer. The first one, the inner Helmholtz plane (IHP), passes through the centres of specifically adsorbed ions (compact layer in the Helmholtz model), or is simply located just behind the layer of adsorbed water. The second plane is called the outer Helmholtz plane (OHP) and passes through the centres of the hydrated ions that are in contact with the metal surface. The electric potentials linked to the IHP and OHP are usually written as $Y2$ and $Y1$, respectively. The diffuse layer develops outside the OHP. The concentration of captions in the diffuse layer decreases exponentially vs the distance from the electrode surface. The hydrated ions in the solution are most often octahedral complexes; however, in the figure, they are shown as tetrahedral structures for simplification.

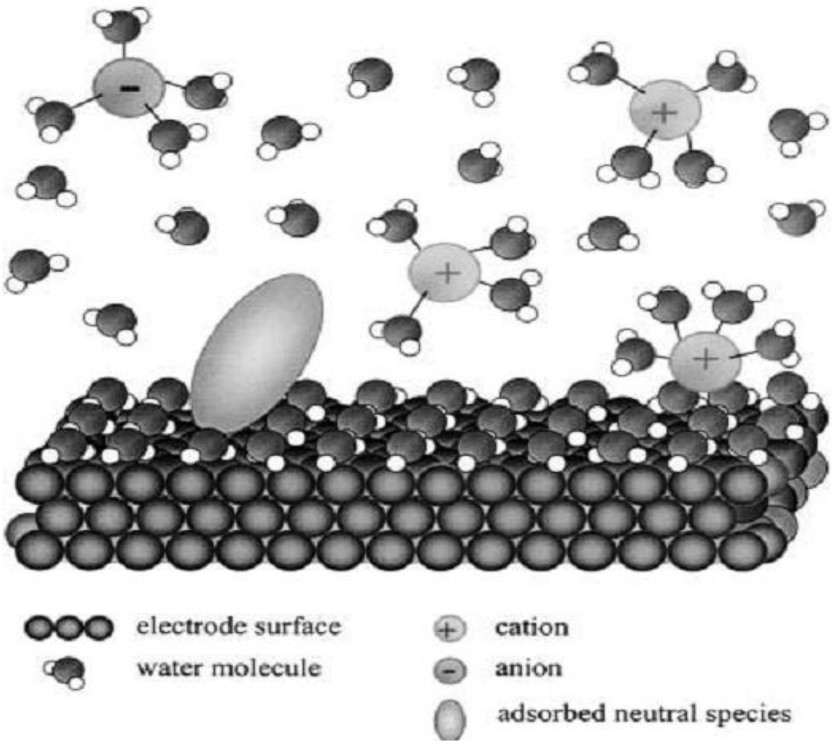

Fig.1.6: General representation of the double layer formed at the metal–electrolyte interface

3.5 Application of electric double layer

The electric field in the electrode–solution interface region is extremely high. The fall-off in the electrical potential between the metal electrode and the electrolyte solution occurs in a very small distance (approximately 3 nm) resulting in an electrical field in the electric double layer as large as 3×10^7 V/cm. Also, the charge that can be accommodated at the surface of the electrode by the specifically and non-specifically adsorbed ions is on the order of 0.1 to 0.2 electrons per atom of metal at the surface; the electric double layer has a very large capacitance of 20 to 50 $\mu C/cm^2$. For a typical difference in potential of 1V between the electrode and the solution, the energy stored in the interfacial capacitance can be as large as 150 kJ/kg. Hence electrochemical capacitance can be used to provide back-up energy to compensate for power failures in electronic devices.

3.6 Potential at zero charge

In electrochemistry, the electrode-electrolyte interface is generally charged. If the electrode is polarizable, then its surface charge depends on the electrode potential. IUPAC Defines the potential at the point of zero charge as the potential of an electrode (against a defined reference electrode) at which one of the charges defined is zero. The potential of zero charge is used for determination of the absolute potential in a given electrolyte.

IUPAC also defines the potential difference with respect to the potential of zero charge as (equation 1.3):

$$E_{pzc} \quad = \quad E - E_0 \qquad\qquad 1.3$$

Where E_{pzc} is the electrode potential difference with respect to the point of zero charge, $E_{0.}$ E is the potential of the same electrode against a defined reference electrode V. E_0 is the potential of the same electrode when the surface charge is zero, in the absence of specific adsorption other than that of the solvent, against the reference electrode as used above, V.

The structure of electrolyte at the electrode surface can also depend on the surface charge, with a charge around the pzc potential. For example, on a platinum electrode, water molecules have been reported to be weakly hydrogen-bonded with "oxygen-up" orientation on negatively-charged surfaces, and strongly hydrogen-bonded with nearly flat orientation at positively charged surfaces.

PZC is a characteristic value of the electrode potential for any metal at which a clean surface of the metal will not acquire an electrical charge when it comes into contact with an electrolyte. The electrolyte, though, must not contain a surfactant. If the electrode potential is positive in relation to the potential of zero charge, then negative ions are attracted to the metal from the solution; if it is negative in relation to the potential of zero charge, then positive ions are attracted. In both cases, the usual tendency of particles of matter to move from the surface to the bulk phase is repressed; that is, the surface tension at the boundary between the metal and the solution is reduced. With a liquid electrode, for example, a mercury electrode, this effect is easily seen through electrocapillary curves, which show the relationship between the potential of the metal meniscus in contact with the electrolyte and the extent of capillary rise or fall. At the potential of zero charge, the surface tension is at a maximum, and the electrical capacitance at the boundary is at a minimum. The potential of zero charge is important in the study of the kinetics of electrode reactions, in the selection of corrosion inhibitors, and in other cases where it is important to consider the adsorption of components on metal surfaces.

4.0 Conclusion

The present Unit revealed that the electric double layer presents an electrochemical phenomenon that is worth examining. Although there are minor conflicts between various models aimed at explaining electric double layer, it is certain that the electric double layer problem is an interracial process that extends within a certain distance from the electrode. Detailed study on microscopic properties of the double layer will reveal more information. However, it is beyond the scope of this course but interesting fact can be found in some literature, referred at the end of this Unit (under references and further reading).

5.0 Summary

The existence of electric double layer in an electrochemical system connects a vital process the presence of charge ions can counter within an electrochemical system. The double layer processes occur within a distant of 0.5 to 100 nm from the electrode. The electric double layer structure and its capacity depend on several parameters such as: electrode material (metals, carbons, semiconductors, electrode porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature. Therefore, altering any of this functions can although the nature of the double layer, which may enhance or counter its useful applications.

The importance of the EDL has led to numerous studies, and many models were proposed in the past. The best known is the Gouy–Chapman model, in which ions are considered as point charges and water is considered as a continuum.

6.0 Tutor-marked assignments

1. What are the parameters that affects the structure of an electric double layer:
2. Given an electrochemical cell, identify the three major zones that exist between an electrode and electrolyte and explain why the concentration of ions in each of the zone is expected to differ.
3. Differentiate between Faradic charge transfer and non Faradic charge transfer. Which of them is common in an electrochemical cell?
4. Briefly describe the importance and limitations of the Stern model on the existent of an electric double layer (Use suitable diagram to support your answer

5. What are the basic applications of electric double layer in the industries?
6. Does the Gouy Chapman layer model of electric double layer offers better explanation than the Stern model? Give reason for your answer.

7.0 References/Further reading

Atkins, P. and De Paula, J. (2010). Atkins'Physical Chemistry.Ninth Edition.Oxford University Press. UK.

Attard, G. A., Hazzazi, O., Wells, P. B., Climent, V., Herrero, E and Feliu, J. M. (2004). On the global and local values of the potential of zero total chargeat well-defined platinum surfaces: stepped and adatommodified surfaces. Journal of Electroanalytical Chemistry 568:329–342

Bogotsky, V. S. (2006). Fundamentals of Electrochemistry, Wiley-Interscience, USA.

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry.5th Edition.Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

Yang, K. and Tsouris, Y. (2004) Electric double layer formation.Dekker Encyclopedia of Nanoscience and Nanotechnology. Dekker. USA.

MODULE 2

Unit 1: Polarization at interface

1.0 **Introduction**

2.0 **Objectives**

3.0 **Main content**

- **3.1** Polarizable and non polarizable interfaces
- 3.2 Polarization of a single electrode
- 3.3 Dependence of activation overpotential on current

4.0 **Conclusion**

5.0 **Summary**

6.0 **Tutor mark assignments**

7.0 **References**

1.0 Introduction

When a small current or potential is applied, the response is in many cases linear. The effective resistance can, however, vary over a wide range. When this resistance is high, we have a polarizable interface, meaning that a small current generates a high potential across it (i.e., the interface is polarized to a large extent). When the effective resistance is low, the interface is said to be non polarizable. In this case a significant current can be passed with only minimal change in the potential.

The concept of the ideal polarizability was first introduced by F. O. Koenig in 1934. Ideally polarizable electrode (also ideal polarizable electrode or ideally polarized electrode), in electrochemistry is an electrode that is characterized by an absence of net current between the two sides of the electric double layer, i.e., no faradic current between the electrode surface and the electrolyte. Any transient current that may be flowing is considered non-faradic but in non-polarizable electrode, a faradic current can freely pass (without polarization).

The classical examples of the two ideal types of electrodes, polarizable and non-polarizable, are the platinum and the silver/silver chloride electrodes, respectively.

2.0 Objectives

At the end of this Unit, student should be able to:

- Explain the concept of polarization in electrochemistry
- State the different types of polarization and overpotentials
- Describe the nature of plots expected for cathodic and anodic polarizations
- Explain the polarization of a single electrode
- Derive Tafel equation for polarization
- Make potentiodynamic polarization plot and calculate Tafel constants from the plot

3.0 Main content

3.1 Polarizable and non-polarizable Interfaces

A non-polarizable electrode is, in effect, a reversible electrode. A good reference electrode is always a reversible electrode. The inverse is not necessarily true. Not every reversible electrode is suitable as a reference electrode. For example, the correct thermodynamic reversible potential of a metal/metal-ion electrode may be hard to reproduce, because of impurities in the metal or complexing agents in the solution, even when the interface is highly non-polarizable. Polarizable interfaces behave differently; their potential is not fixed by the solution composition, and it can be changed at will over a certain range, depending on the metal and the composition of the solution it is in contact with it. For such a system the potential may be viewed as an additional degree of freedom in the thermodynamic sense, as used in the Gibbs phase rule.

To be sure, a so-called non-polarizable interface can be polarized by passing a significant current through it. This, however, alters the concentration of both the reactant and the product at the electrode surface (without changing significantly their bulk concentrations). The potential developed across the interface will be in agreement with the Nernst equation, as long as the concentrations used are the surface concentrations, which depend on the current passing across the interface.

In order to further gain in-depth knowledge into the concept of polarization, let us see what happens to current in an electrochemical cell at equilibrium. In doing this, we write an equilibrium cell equation for the cell given in Fig. 2.1 as follows:

$$M^{n+} = M + ne^- \qquad 3$$

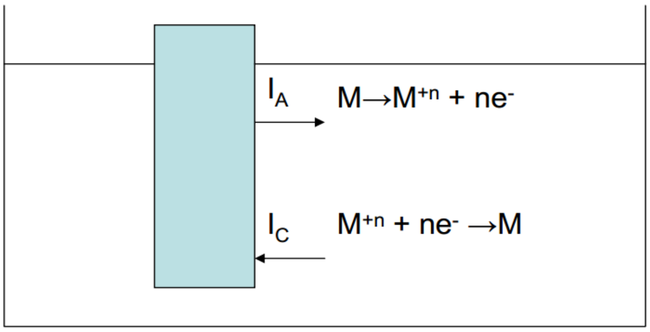

Fig. 2.1: Reactions in a single electrochemical electrode

The current flow can be divided into cathodic and anodic current (i.e, I_A and I_C) and at equilibrium, $I_A = I_C = I_0$. I_0 is called exchange current density. I_0 has been found to depend on the surface of the electrode. For example, for the electrochemical system defined as:

$$2H^+ + 2e^- = H_2$$

experimental value of I_0 is found to be 10^{-12} and 10^{-3} A cm^2 on mercury and platinum electrode respectively.

3.2 Polarization of a single electrode

Consider equation 2.1, if we disturb the equilibrium by pumping current to the system, the equilibrium will proceeds faster in the cathodic reaction direction (equation 2.2) and the potential will become more negative (see Fig. 2.2). In this case, $I_C >>> I_A$ and the plot of E versus I slopes downward

$$M^{n+} + ne^- \rightarrow M \qquad 2.1$$

On the other hand, if we take away current from the equilibrium reaction (equation 3), the reaction will proceed faster in the anodic direction and the potential will become more positive (equation 5). In this case, $I_A >>> I_B$ (see Fig. 2.3)

$$M \rightarrow M^{n+} + ne^- \qquad 2.2$$

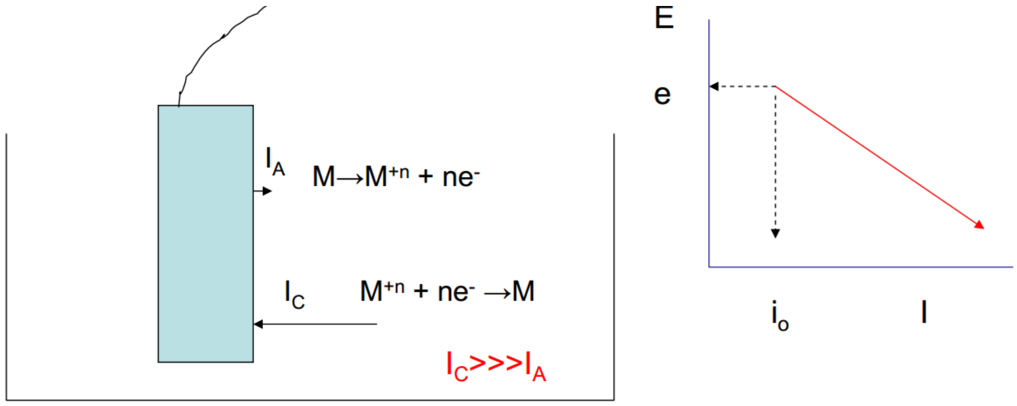

Fig. 2.2: Anodic polarization in a single electrode system

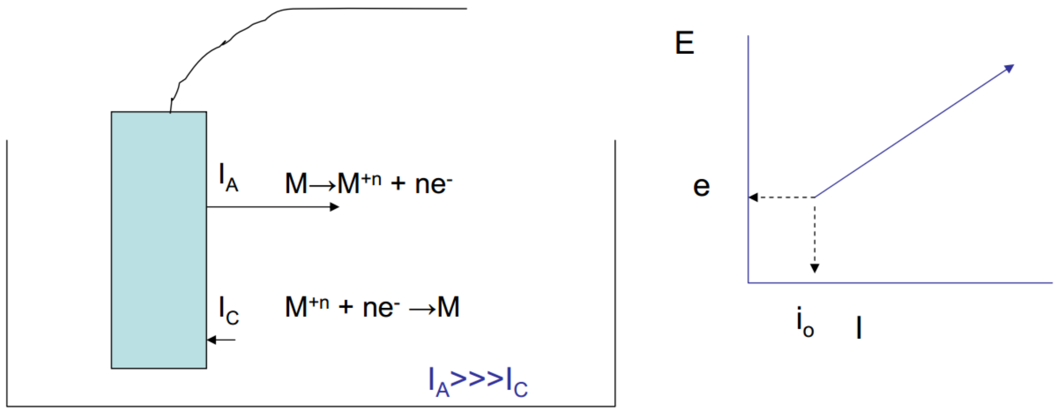

Fig. 2.3: Cathodic polarization in a single electrode system

In Figs. 2.2 and 2.3, E denotes the electrode potential while e stands for the equilibrium potential. The change in electrode potential (E) from the equilibrium potential is called polarization. The difference between E and e is called overvoltage that is,

$$\eta = E(i) - e \qquad 2.3$$

For cathodic polarization, E < e and η_C is negative (equation 2.4) but for anodic polarization, E > e and η_A is positive

$$\eta_C = E(i) - e \qquad 2.4$$

We have just discussed polarization of a single electrode. However, a typical electrochemical cell consists of two electrodes (anode and cathode), indicating that combined effects of anodic and cathodic polarizations must be examined. Generally, there are two types of polarization in an electrochemical cell, namely concentration polarization (η_C) and activation polarization (η_{act}). Activation polarization is caused by charge transfer across the electrode/electrolyte interface while concentration polarization is caused by changes in the ions concentration near the electrode/electrolyte interface. The sum of η_C and η_{act} gives the total polarization across the electrode, thus,

$$\eta = \eta_C + \eta_{act} \qquad 2.5$$

3.3 Dependence of activation overpotential on current: Tafel law

In 1905, Tafel (1862-1981) found that for most electrode reactions, the activation overpotential (η_{act}) is linearly proportional with the log of the current as follows,

$$\eta_{act} = \beta \log(i_o) + \beta log(i) = \beta log\left(\frac{i}{i_o}\right) 2.6$$

For anodic and cathodic polarizations, equation 2.6 can be simplified to equations 2.7 and 2.8 respectively,

$$\eta_{act,a} = \beta_a \log(i_o) + \beta_a log(i_a) = \beta_a log\left(\frac{i_a}{i_o}\right) \qquad 2.7$$

$$\eta_{act,c} = \beta_c \log(i_o) + \beta_c log(i_c) = \beta_c log\left(\frac{i_c}{i_o}\right) \qquad 2.8$$

β_a and β_c are called Tafel constants. Generally, $\beta = \frac{2.3RT}{\propto nF}$, where $\alpha \approx 0.5$.

Most often, activation polarization is normally studied by using an electrochemical instrument that is able to generate data for the variation of electrode potential with current. Results obtained from such studies are normally treated graphically. A typical plot of this nature (for the reaction, $M^{n+} + ne^- = M$) is shown in Fig. 2.4. It can be seen from Fig.2.4 that Tafel constants can be obtained from the slopes of the cathodic and anodic arms of the plot. A plot of this nature is called potentiodynamic polarization plot. Specific example of potentiodynamic polarization curve for the system, $2H^+ + 2e^- = H_2$, is presented in Fig. 2.5. For this reaction at equilibrium, no current flows and the reaction potential is 0 V but at standard condition, i_o = 1 mA/cm^2. If current is allowed to flow, the potential E, changes and the overpotential can be calculated, using Tafel equation (equation 2.9), thus

$$\eta_{act,a} = \beta_a log\left(\frac{i_a}{i_o}\right) = 0.1 log\left(\frac{10}{1}\right) = 0.1\,V \qquad 2.9$$

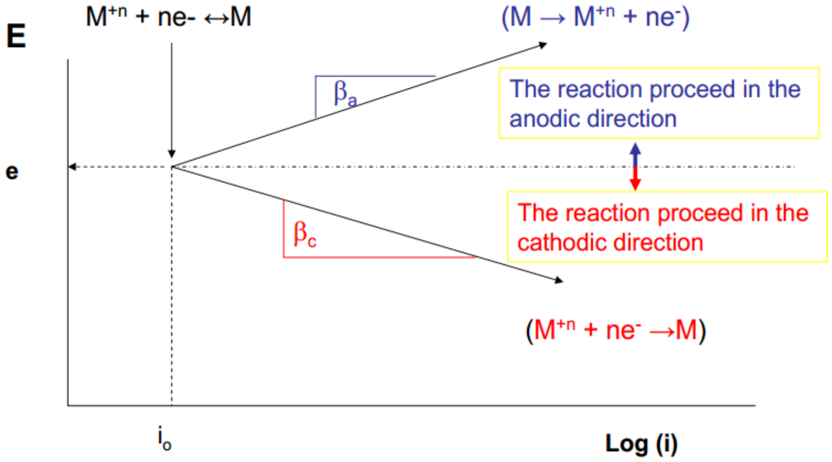

Fig. 2.4: Typical pattern of plot for the variation of E with log(i)

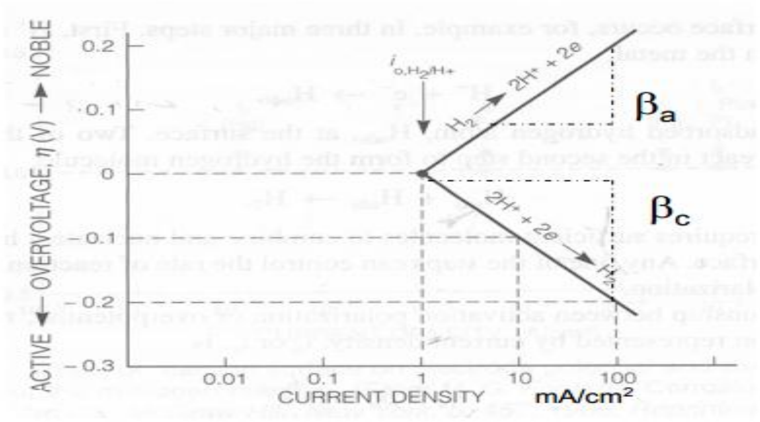

Fig. 2.5: Plot of E versus log(i) for the reaction, $2H^{+} + 2e^{-} = H_2$

4.0 Conclusion

Polarization is a concept that has led to the progress of numerous industrial phenomena. Corrosion is perhaps one of the most widely studied fields using the concept of polarization. Corrosion is an electrochemical process involving the corrosion of the anode (where oxidation takes place). Instrumentation in corrosion using polarization theory involves the production of linear polarization curve and potentiodynamic polarization curve. Several successes have been recorded on the use of polarization technique to study the inhibition of the corrosion of metals such as mild steel, aluminium, etc. Further details on the use of polarization techniques on corrosion are provided in the journal references provided at the end of this Unit.

5.0 Summary

The essential theory in polarization of electrochemical interphases is the one that has been presented by Tafel. It should be noted that several parameters can be deduced from Tafel plots. For example, the slopes of the anodic and cathodic plots give the values of β_a and β_b respectively. If we extrapolate the point of interception of the two plots to the y-axis and x-axis, we have the potential and the current density respectively.

Tutor-marked assignments

1. Differentiate between polarizable and non polarizable electrode
2. In what ways can the cathode and the anode be polarised. Use suitable equation to explain your answer
3. What is the difference between over voltage arising from cathodic and anodic polarization respectively
4. Briefly describe how you can estimate Tafel constant for anodic and cathodic polarization, given that exchange current density, anodic current and cathodic current are provided. Draw suitable diagram to support your explanation.
5. What is the difference between polarization of a single electrode and polarization of a two electrode system?

7.0 References/Further reading

Atkins, P. and De Paula, J. (2010). Atkins' Physical Chemistry.Ninth Edition.Oxford University Press. UK.

Eddy, N. O., Momoh-Yahaya, H. and Oguzie, E. E.(2014). Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. Journal of Advanced Research. DOI:.101:215-14- 00237-0

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry.5th Edition.Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

UNIT 2: Verification of Tafel Equation: Butler-Volmer law

1.0 Introduction

Prof. Juluis Tafel was a lecturing organic Chemistry at The Chemical Institute, Wurzburg University, Germany up to 1893. However, after 1893 he lectured physical and general chemistry. By German tradition, this would include lots of electrochemistry, and lots of experimentation. With strychnine reduction, Tafel had truly turned electrochemist. A careful observer, Tafel soon was able to summarize his major and rather far-reaching general deductions from his experimental work. He is regarded as one of the fathers of electrochemistry

In this unit, we shall examine some of the basic findings of Tafel laws and the modification and application of his findings.

2.0 Objectives

At the end of this unit, student should be able to:

1. Describe the irreversible behaviour of an electrode.
2. Describe the mechanism of electron transfer to an electrode.
3. Describe the mechanism of electron transfer to an electrode
4. Determine the current density.
5. Derive the Butler Volmer equation
6. Verify the Tafel equation
7. Interprete Evan’s diagram

3.0 Main content

3.1 Derivation of Butler Volmer equation

Tafel equation governs the irreversible behaviour of an electrode. To understand this we can consider the general mechanism of electron transfer to an electrode. Consider an electrolyte in which an inert or noble electrode is kept immersed. It is called working electrode, (WE). Also assume that an oxidised and a reduced species are present near the electrode and exhibit the following electron transfer reaction.

$$\text{Ox} + \text{ne}^- = \text{Rx} \qquad 2.10$$

"Ox" is the oxidise and "Rx" is the reduced species present at equilibrium and is stable in the solution. Let us assume that no other electron transfer reaction other than the above. Let the concentration of Ox and Rx be C_o and C_R respectively and they are very low. An inert electrolyte is also present to minimise IR drop. Along with WE, a reference electrode RE is also kept immersed, to form the cell. Since the potential of RE is constant, variation in cell emf is the variation in WE and vice versa.

At the thermodynamic equilibrium of the system no net current flows across RE and WE, no chemical reaction takes place and hence the composition of the solution remains unchanged. The potential of the working electrode will be its equilibrium potential E_e and by applying the Nernst equation, we have,

$$E_e = E_e^0 + \frac{nF}{RT} ln \left[\frac{C_O}{C_R}\right] \qquad 2.11$$

Where E_e^O is the standard or formal reversible potential and is constant. E_e depends on the ratio of $[C_O/C_R]$. The bracketed term should be in terms of activity and not molar concentration; but at low concentration the replacement is error free. The equilibrium mentioned above is dynamic. Though no net current flows across the electrodes, both reduction and oxidation takes place at equal rate, so that the composition of the electrolyte does not change. The dynamic flow of electrons or charge in both directions can be written in terms of current densities as follows.

$$I_O = I_A = I_C \qquad 2.12$$

where I_A is anodic and I_C is cathodic current densities. By convention, anodic current density is given a positive sign and cathodic current density, a negative sign. I_O is known as exchange current density. It may be defined, as "the flow of charge or electrons across an electrochemical system in equilibrium". Its value normally is very low, of the order 10^{-8} A. It refers to the extent of both oxidation and reduction that occurs.

The equilibrium situation at an electrode is characterised by equilibrium potential and exchange current density. For the reaction to have practical significance, a net current should flow and a net reaction either oxidation or reduction should occur. For this the kinetic aspect of the system must be considered. It is to be recalled that thermodynamics fixes the direction and kinetics determines the rate. For this, let us apply an external potential to WE, more negative than E_e. This causes an increase in cathodic current and a net quantity of Ox will be reduced to Rx. The value of the ratio $[C_O/C_R]$ at the electrode surface will diminish. The magnitude of net cathodic current and the time for the new value of $[C_O/C_R]$ takes to achieve depend on the rate or the kinetics of the electron transfer reaction. The net cathodic current will be due to the increase in partial cathodic current (I_C) and a decrease in partial anodic current (I_A) at this new potential. Hence reversible condition changes to irreversible condition. This is achieved by applying a more -ve potential or excess potential than $E_{e,}$ which is known as over potential. Conversely, it can be argued that if WE is made more positive than E_e by applying external potential more positive than E_e, a net anodic current will flow through the cell. Generally, at the equilibrium potential, no net current

$$E_e \quad \leftrightarrow I = I + I_A = 0 \qquad 2.13$$

Negative to I_A, , a net cathodic current: $E_e \quad \leftrightarrow I = I + I_A < 0$ and positive to I_A: $E_e \quad \leftrightarrow I = I + I_A > 0$The famous Butler-Volmer equation is expressed as:

$$I \;=\; I_O \left\{ exp\left[\frac{\alpha_A nF\eta}{RT}\right] - exp\left[-\frac{\alpha_B nF\eta}{RT}\right]\right\} \qquad 2.14$$

Equation 16 reveals that the measure current density is a function of overpotential (η), exchange current density (I_O) and anodic and cathodic transfer coefficients (α_A and α_B respectively). Generally, $\alpha_A + \alpha_B = 0$. However, for most reactions, $\alpha_A + \alpha_B = 0.5$. Equation 2.14 further reveals that the current density at any over potential is the sum of cathodic and anodic current densities. At the extreme condition of over potential being highly negative, cathodic current density increases while anodic current density becomes negligible. At this stage, the first term in Butler-Volmer equation (equation2.14) becomes negligible. The equation can be written as:

$$I \;= -I_C \;=\; I_O \left\{ exp\left[-\frac{\alpha_C nF\eta}{RT}\right]\right\} \qquad 2.15$$

When the over potential is higher than above 52 mV, this equation shows that the increase in current is exponential with over potential. The current also depends on I_O. Equation 2.14 may also be written as:

$$logI - logI_C = logI_O - \frac{\alpha_C nF\eta}{RT} \qquad 2.16$$

Equation 2.16 is called cathodicTafel equation. Similarly, at positive overpotential higher than 52 mV, anodic current density is much higher than cathodic and the cathodic current density become negligible, hence we have:

$$I = I_A = I_O\left\{exp\left[\frac{\alpha_A nF\eta}{RT}\right]\right\} \qquad 2.17$$

$$logI + logI_A = logI_O + \frac{\alpha_A nF\eta}{RT} \qquad 2.18$$

Equation 2.18 is the anodic Tafel equation. When log I values are plotted against over potential, the straight line obtained is Tafel plot. These offer simple method for experimentally determining I_O, transfer coefficients.

3.2 Experimental Determination of *I* and Tafel Plot

The test electrode is kept immersed in its salt solution. The solution should be very dilute so that the concentration near the surface of the electrode does not differ too much from the bulk concentration. A calomel electrode is kept very close to the test electrode. An inert electrode is also taken which serves as the counter electrode. A DC potential is applied across the test and the counter electrodes, making the test electrode negative. This establishes a potential across the test and the reference electrodes which is read by a very sensitive voltmeter connected in the circuit. From this value the rest potential is subtracted to get the applied potential component on the test electrode. An ammeter connected in series reads the current passing through the circuit. The applied potential is increased which increases the over potential on the cathode (test electrode is made more negative) and the corresponding current value is measured (ammeter reading). In this way the current values are taken for several over potential values making test electrode more and more negative. The log values of these current values are plotted against the over potential on one side.

In the next step the test electrode is connected to the positive terminal and the counter to negative. As done earlier the current is measured for various over potential values and plotted against them on the other side of the graph.

3.3 Significance of Tafel Plots

1. The point of intersection on the Y axis of the extrapolated graph gives the value of I_0, the exchange current density, which is otherwise very difficult to determine.
2. The transfer coefficients can be determined; from the anodic slope, α_A and from cathodic slope α_C can be determined. This value is very important in industrial practice. This determines the potential that is to be applied to affect the desired rate of reduction or oxidation.
3. Knowing the value of transfer coefficient for a reaction the number of electrons, n, for an unknown reaction can be determined. This reflects on the mechanism of the reaction; that is how many electrons are involved in that step. Whether the reaction is single step or multi step is revealed by this value.
4. The effect of α_C on current density is shown in Fig. 2.6.

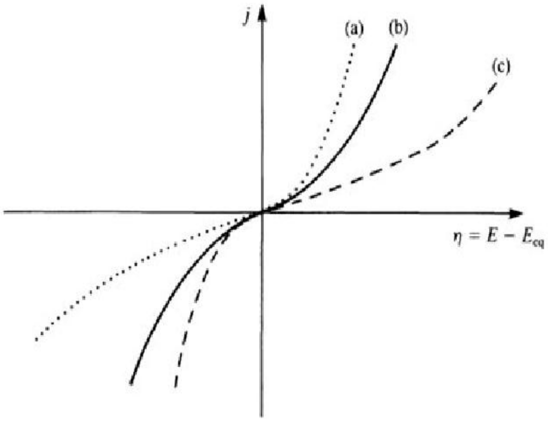

Fig. 2.6: The effect of a on the current density, j. (a) α_C = 0.25: oxidation favoured; (b) α_C = 0.50: symmetric (c) α_C = 0.75: reduction favoured

As cathodic transfer coefficient value increases reduction is favoured and oxidation is not favoured and vice versa for anodic transfer coefficient. The transfer coefficients depend on the pH of the medium; in acidic conditions (low pH) reduction is favoured which is revealed by an increase inα_C

3.4 Concentration over potential

At high currents, cations involved in cathodic reactions are depleted due to metal ion reduction (i.eM^{n+} + $ne^{-} \rightarrow$ M). Diffusion and convection are two major mass transport processes that are responsible for transporting cations from the bulk solution to the electrode surface. The ion concentration near the surface of the electrode depends on diffusion while the process of convection controls the transportation of ions from the bulk solution. If the concentration of the cations vary from near the surface concentration (C_S) to the bulk concentration (C_B) across the cathode over a distance (δ), we define the concentration gradient as follows,

$$Concentration\ gradient = \frac{dC}{dx} = \frac{(C_B - C_S)}{\delta} \qquad 2.19$$

From Fick's first law, current density (J) is defined as the product of concentration gradient and diffusion coefficient (D_{ion}). Therefore,

$$J = D_{ion} \frac{(C_B - C_S)}{\delta} \qquad 2.20$$

Also, cathodic current is defined as nFJ and by substitution into equation 21, cathodic current becomes,

$$nFJ = nFD_{ion} \frac{(C_B - C_S)}{\delta} \qquad 2.21$$

However, maximum current is obtained when the concentration of ions at the surface is equal to zero (i.e $C_S = 0$) and the current obtained at the cathode under this condition is called limiting cathodic current (i.e$i_{max, C} = i_L$). Hence equation 2.21 becomes,

$$i_L = nFD_{ion} \frac{C_B}{\delta} \qquad 2.22$$

Two extreme conditions can be linked to C_B and C_S and they can be resolved using the Nernst equation. The first condition is before current flow while the second condition is after current flow. Application of the Nernst equation to these two conditions yields equations 2.23 and 2.24 respectively

$$e_i = e^0 + \frac{2.3RT}{nF} log\left(\frac{[C_B]}{1}\right) \qquad 2.23$$

$$e_f = e^0 + \frac{2.3RT}{nF} log\left(\frac{[C_S]}{1}\right) \qquad 2.24$$

From the above, concentration cathodic overpotential would be defined as e_f - e_i and is equal to

$$\eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log \left[1 - \frac{i_C}{i_L}\right] \qquad 2.25$$

From equation 2.25, we can examine the effect of i_L on $\eta_{C,Con}$ as follows,

If $i_c << i_L$, then the ratio, $\frac{i_C}{i_L}$ $will\ tend\ to\ 0\ and\ \eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log[1]$, will be equal to 0

If $i_c \approx i_L$, then the ratio, $\frac{i_C}{i_L}$ will be equal to unity and $\eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log[0]$, will be equal to infinity.

3.5 Total polarization for a single electrode

In summary, total polarization can be separated into total anodic and total cathodic polarization as follows,

Total anodic polarization: $\eta_{T,a} = \eta_{act,a} = \beta_a log\left(\frac{i_a}{i_0}\right)$

Total cathodic polarization: $\eta_{T,C} = \eta_{act,C} + \eta_{con,C} = \beta_C log\left(\frac{i_C}{i_0}\right) + \frac{2.3RT}{nFD_{ion}} log\left[1 - \frac{i_C}{i_L}\right]$

The above concept is can be summarised graphically as shown in Fig. 2.8, which represents, Evans diagram. In summary, activation polarization can occur in the anode and the cathode while concentration polarization is common at the cathode.

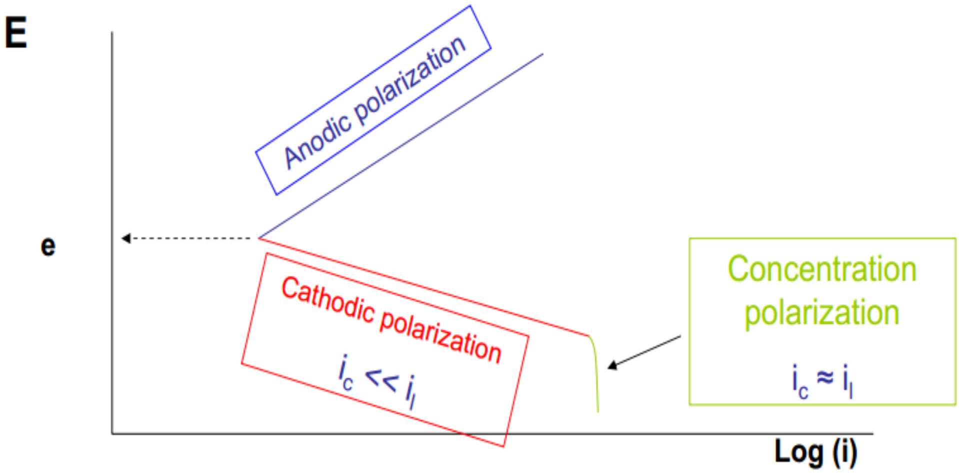

Fig.2.8: Evans diagram showing anodic and cathodic polarizations

4.0 Conclusion

The most interesting aspect of polarization is that what occurs in the cathode may not be exactly the same, at the anode. Therefore anodic and cathodic polarization should first be considered separately and the total polarization is the some of the two. Evans diagram summarises what happened to total polarization. It is worth observing that polarization can be perfectly analysed graphically, once the data has been obtained.

5.0 Summary

This section summarises the chemistry behind the major types of polarization and supports them with appropriate modes. The section greatly bridged the gap between practical and theoretical aspect of polarization. It is indeed interesting to study this unit with understanding.

6.0 Tutor-marked assignments

1. Use the Nernst equation to describe the dependence of the electrode potential of an electrochemical system on the concentrations of the oxidized and the reduced species.
2. State Fick's first law of diffusion, given that C_A and C_B denote the concentrations of diffusing species at the bulk and surface respectively. Under what condition, can we obtain a mathematical equation that relates these concentrations with the limiting current (i_L)?
3. Write an expression that relates cathodic over-potential to the cathodic current (i_C) and the limiting current (i_L). From the expression, state what will happened to the overpotential if (a) $i_c > i_L$ (b) $i_C < i_L$ (c) $i_C = i_L$
4. Write an expression for (a) total anodic polarization (b) total cathodic polarization (c) Sketch the Evans diagram to show the expected graphs for the different polarization types.
5. Highlight briefly the contribution of Tafel and Butker-Volmer to the development of electrochemistry. In what way did Butler-olmer improve Tafel equation?

7.0 References/Further reading

Atkins, P. and De Paula, J. (2010). Atkins'Physical Chemistry.Ninth Edition.Oxford University Press. UK.

Eddy, N. O.,Momoh-Yahaya, H. and Oguzie, E. E.(2014).Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. Journal of Advanced Research. DOI:.101:215-14- 00237-0

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry.5th Edition.Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

MODULE 3:

Unit 1: Mass Transport

1.0 Introduction

All transports (including mass transport) are based on the fact that the rate of change for a system's physical property is a function of the spatial gradient of the property. Generally, the concept of transport involves the changing of a system's property, in response to a non-equilibrium distribution of the property. One of the fundamental requirements for transportation is that there should exist a spatial distribution of the system's property, which is different from that at equilibrium.

The quantity transferred through a given area in a given amount of time is called flux. Generally, when a spatial imbalance or gradient exists for a given property, flux will occur. Generally, for a given property, flux is defined as expressed in equation 3.1:

$$J = -k\frac{d(property)}{dx} \qquad 3.1$$

where J is the flux. The derivative represents the spatial gradient of the quantity of interest (for example, mass or energy). The negative sign indicates that the flux occurs in the opposite direction of the gradient; therefore flux will lead to the reduction in the gradient, if external force is not applied to maintain the gradient. In equation 3.1, the term k is called the transport coefficient.

2.0 Objectives

At the end of this unit, students should be able to show understanding of:

- the concept of mass transport as it applies to electrochemistry
- the concept of flux in mass transport
- the three major types of mass transport in electrochemistry
- the concept of rotating disc electrode and the derivation of Levich law
- the application of Levich equation in electrochemistry

3.0 Main content

3.1 Mass transport in electrochemical system

In electrochemistry, the most common and significant transport process is the mass transport and shall be singled out for discussion in this Unit.

An electrode reaction proceeding at a finite rate involves movement of reacting materials between the electrolyte and the solution surrounding it. In the absence of fluid turbulence, ions can be transferred from solution to an electrode by three principal mechanisms:

i. Migration: Movement of charge body under the influence of an electric field
ii. Diffusion: Movement of a species under the influence of concentration gradient
iii. Convection: This results from Stirring or hydrodynamic transport

For a given species, the rate of transfer in the y direction per unit area perpendicular to y at any point in the fluid, can be expressed according to equation 3.2

$$N_t = cU\frac{d\phi}{dx} - D\frac{\partial x}{\partial y} + Vc \qquad 3.2$$

where N_t is the total rate of transfer, c is the concentration of a given specie, U is the mobility, ϕ is the potential, y is the distance in the direction of the transfer, D is the diffusion coefficient, V is the velocity of bulk fluid movement in the direction of the transfer. The first, second and third terms of equation 3.3 represent the contributions from migration, diffusion and convection respectively. In the bulk only the ions are engaged in the charge transport.

3.2 Transport of ions in electrolytes

At the anode, there is excess of positive ions arising from build-up of positive charges. Similarly, at the cathode, there is a build-up of negative charges, leading to excess of negative charges. The building up of ions leads to ionic transport. In this case, positive charges move from the anode to the cathode while negative charge moves from the cathode o the anode. The process where positive charges move to the cathode (and negative charges to the anode), is called ion transport. The fractions of current carried by the positive and negative ions are given by their transport numbers (t_+ and t_-). Each mole of current that is passed through an electrochemical cell corresponds to 1 mole of electrochemical charge at each electrode, which indicates that the amount of ions transported in the electrolyte is also equal to 1 mole (i.e, , $t_+ + t_- = 1$). The transport numbers of ions is strongly influenced by the conductance of an electrolyte, which can be expressed as follow,

$$L = \frac{kA}{l} \qquad 3.3$$

where L is the conductance in Siemens (S), k is the conductivity in S/cm, A is the surface area of the electrode in cm^2 and l is the thickness or length of electrolyte matrix in cm.

It has been found that the conductivity of an electrolyte is proportional to the following parameters:

i. The mobility of the ion
ii. The concentration of the ion
iii. Charge of the ion.

Mobility is defined as the limiting velocity of an ion in an electric field of unit strength. Therefore if the strength of an electric field is E, then the force exerted is given by

$$F = eEz = \frac{ze\Delta\phi}{L} \qquad 3.4$$

where e is the electronic charge, z is the charge of the ion and $\Delta\phi$ is the potential difference between two electrodes separated by a distance L. However, in an electrochemical system, ions in motions experience an opposing frictional force, which can be expressed according to Stokes law:

$$F_{fric} = 6\pi\eta rv \qquad 3.5$$

Where η is the viscosity of the electrolyte, r is the radius of the ion and v is the velocity of the ion in solution. A system of this type attains a terminal velocity when the accelerating (equation 3.5) and the retarding forces (equation 3.6) counter-balance each other. This terminal velocity is termed the mobility (u) when the electric field strength is unity:

$$u = \frac{ze}{6\pi\eta} \qquad 3.6$$

The mobility of ion can therefore be expressed according to equation 3.7:

$$k = F\Sigma z_i C_i u_i \qquad 3.7$$

The transport number of a cation or anion can then be expressed as the ratio of the contribution made by the cation or anion to the total current carried in solution. Thus,

$$t_i = \frac{z_i u_i C_i}{\Sigma z_i C_i u_i} \qquad 3.8$$

3.3 Rotating disk electrode (RDE) theory: the Levic equation

The general theory describing the rotating disk electrode was originally developed by Dr. Benjamin Levich in his landmark book called physicochemical hydrodynamics (Prentice-Hall). In 1962, this book was translated from Russian to English, and researchers in the United States and the United Kingdom rapidly built upon Dr. Levich's seminal work. Dr. Stanley Bruckenstein's laboratory at the University of Minnesota (and later at the University of Buffalo) helped to spread the theory and application of the rotating disk electrode to many other electroanalytical chemists, including Dr. John Albery (Oxford University) and Dr. Denis Johnson (Iowa State University). Subsequent generations of researchers expanded on this initial work until the rotating disk electrode became a mature tool for probing electrochemical reaction kinetics.

The theory

The laminar flow at a rotating disk electrode conveys a steady stream of material from the bulk solution to the electrode surface. While the bulk solution far away from the electrode remains well-stirred by the convection induced by rotation, the portion of the solution nearer to the electrode surface tends to rotate with the electrode. Thus, if the solution is viewed from the frame of reference of the rotating electrode surface, then the solution appears relatively stagnant. This relatively stagnant layer is known as the hydrodynamic boundary layer, and its thickness (δ_H) can be approximated to be equal to equation 3.9

$$\delta_H = 3.6\left(\frac{v}{\omega}\right)^{1/2} \qquad 3.9$$

in terms of the kinematics viscosity of the solution (ν) and the angular rotation rate (ω = 2πf/60), where f is the rotation rate in revolutions per minute). In an aqueous solution at a moderate rotation rate (~1000 RPM), the stagnant layer is approximately 300 to 400 μm thick. Net movement of material to the electrode surface can be described mathematically by applying general convection-diffusion concepts from fluid dynamics. Mass transport of material from the bulk solution into the stagnant layer occurs by convection (due to the stirring action of the rotating electrode). But after the material enters the stagnant layer and moves closer to the electrode surface, convection becomes less important and diffusion becomes more important. Indeed, the final movement of an ion or molecule to the electrode surface is dominated by diffusion across a very thin layer of solution immediately adjacent to the electrode known as the diffusion layer.

The diffusion layer is much thinner than the hydrodynamic layer. The diffusion layer thickness (δ_{diff}) can be approximated according to equation 3.10:

$$\delta_{diff} = 1.61(D_F)^{1/3}v^{1/6}\omega^{-1/2} \qquad 3.10$$

in terms of the diffusion coefficient (D_F) of the molecule or ion. For a molecule or ion with a typical diffusion coefficient ($D_F \cong 10^{-5}$ cm^2/sec) in an aqueous solution, the diffusion layer is about twenty times thinner than the stagnant layer ($\delta_{diff} \cong 0.05\ \delta_H$).

The first mathematical treatment of convection and diffusion towards a rotating disk electrode was given by Levich. Considering the case where only the oxidized form of a molecule (or ion) of interest is initially present in the electrochemical cell, the cathodic limiting current (i_{LC}) observed at a rotating disk electrode is given by the Levich equation

$$i_{L,C} = 0.620nF(D_0)^{\frac{2}{3}}v^{\frac{-1}{6}}C_0\omega^{\frac{1}{2}} \qquad 3.11$$

in terms of the concentration (C_O) of the oxidized form in the solution, the Faraday constant (F = 96485 coulombs per mole), the electrode area (A), the kinematic viscosity of the solution (ν), the diffusion coefficient (D_O) of the oxidized form, and the angular rotation rate (ω). On the other hand, when the solution initially contains only the reduced form, the Levich equation for the anodic limiting current (i_{LA}) can be written as

$$i_{L,A} = 0.620nF(D_R)^{\frac{2}{3}}v^{\frac{-1}{6}}C_R\omega^{\frac{1}{2}} \qquad 3.12$$

where the concentration term (C_R) and diffusion coefficient (D_R) are for the reduced form rather than the oxidized form.

3.4 Applying the Levich equation

A Levich study is a common experiment performed using a rotating disk electrode in which a series of voltammograms is acquired over a range of different rotation rates. For a simple electrochemical system where the rate of the half reaction is governed only by mass transport to the electrode surface, the overall magnitude of the voltammogram should increase with the square root of the rotation rate (Fig. 3.1)

The currents measured during a Levich study are usually plotted against the square root of the rotation rate on a graph called a Levich plot. As predicted by the Levich equation, the limiting current (represented by the circular filled legend) increases linearly with the square root of the rotation rate (with a slope of $0.620\ n\ F\ A\ D^{2/3}\ \nu^{-1/6}\ C$) and the line intercepts the vertical axis at zero. It is common to choose a set of rotation rates that are multiples of perfect squares (such as 100, 400, 900, 1600 RPM, etc.) to facilitate construction of this plot.

If the electrochemical half-reaction observed during a Levich study is a simple and reversible half reaction (with no complications due to sluggish kinetics or coupled chemical reactions), then the shapes of the mass-transport controlled voltammograms will be sigmoidal regardless of the rotation rate. This means that the current observed at any given potential along the voltammogram will vary linearly with the square root of the rotation rate (see plot of current versus rotation rate in Fig.16). But, it is important to remember that the Levich equation only applies to the limiting current, not to the currents along the rising portion of the sigmoid. Because the Levich equation only applies to the limiting current, the results from a Levich experiment are typically presented as a simple plot of the limiting current versus the square root of the rotation rate as shown in Fig. 3.2.

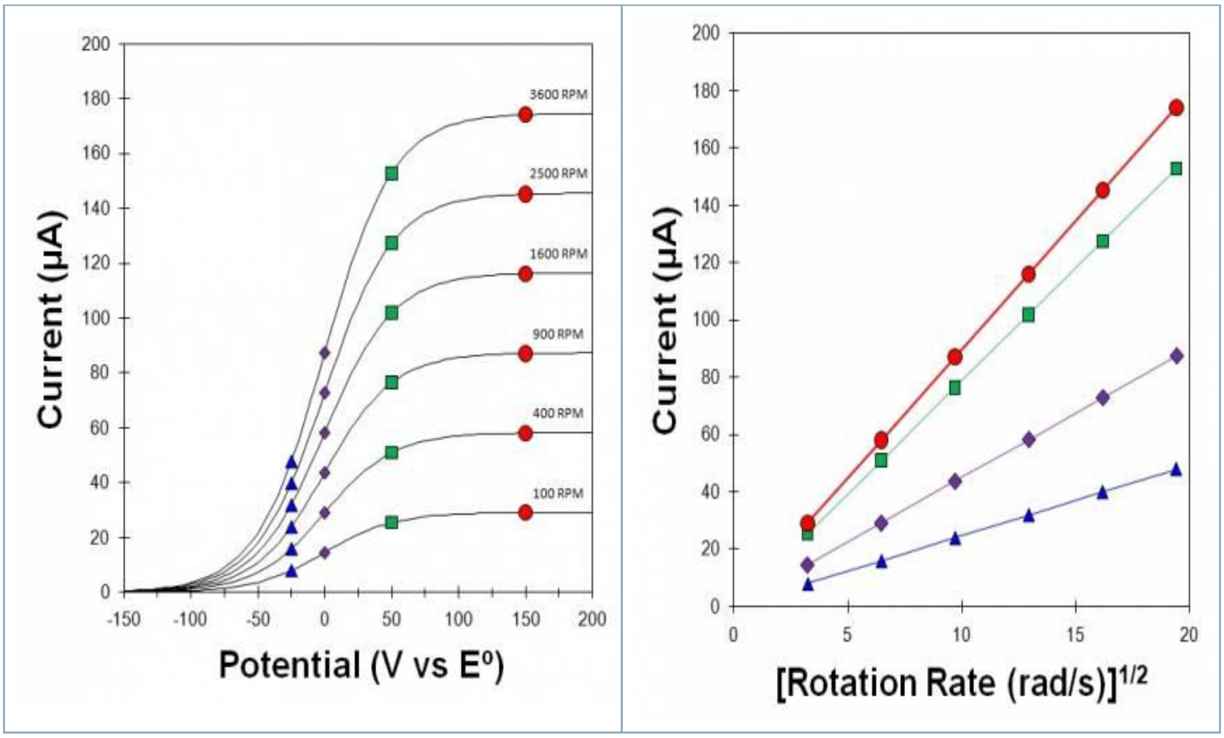

Fig. 3.1: Levich Study – Voltammograms at various rotation rates

The levich equation can be re-arranged to the form expressed below:

$$\frac{1}{i_L} = \left(\frac{1}{0.620nFAD^{\frac{2}{3}}v^{\frac{-1}{6}}C}\right)\omega^{\frac{-1}{2}} \qquad 3.13$$

From equation 3.14, a plot of reciprocal current versus the reciprocal square root of the angular rotation rate should give a straight line called a Koutecky-Levich plot as shown in the right hand plot in Fig. 3.2. It should be noted that for a simple and reversible half reaction with no complications the data fall along a straight line that intercepts the vertical axis at zero. If the line intercepts the vertical axis above zero, however, this is a strong indication that the half-reaction is limited by sluggish kinetics rather than by mass transport.

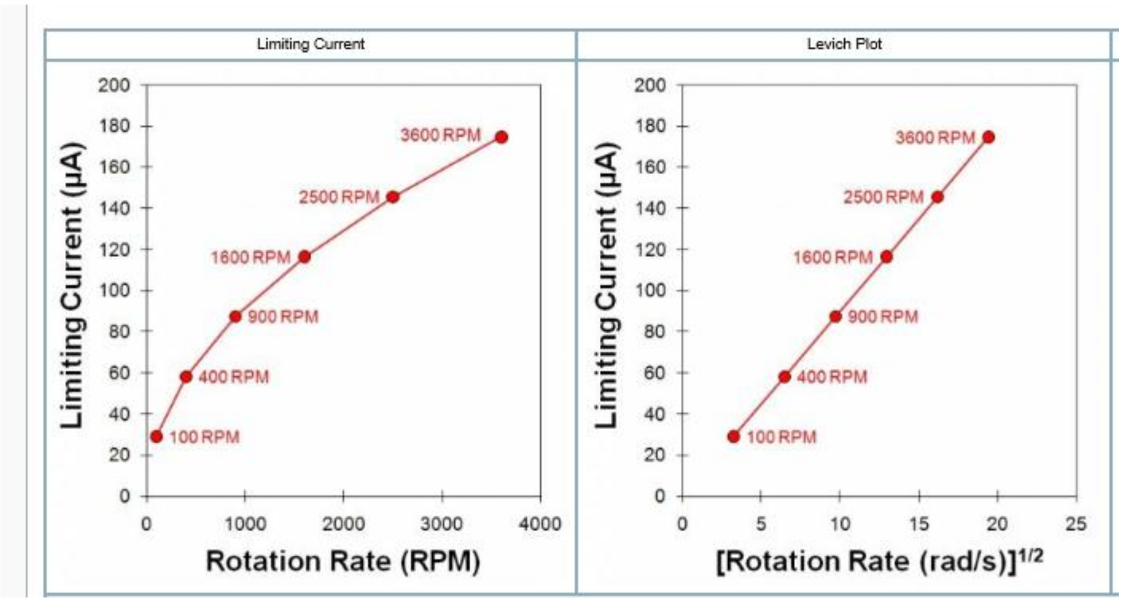

Fig. 3.2: Levich Study – Limiting Current versus Rotation Rate

4.0 Conclusion

Mass transport is an essential process in electrochemical systems. Materials can be transported by migration (basically charge), diffusion and convection. It is significant to note that mass transport by migration and diffusion dominates most electrochemical systems compared to convection. In order to encourage mass transport by convection, some external forces (such as thermal agitation) must be introduced into the system. Relevant laws in the field of mass transport are the Fick's first and second laws. The Levich law is another law that explain some mechanism of mass transfer. Although the Levich law is derived based on a rotating disc electroscope, it is significant in analytical electrochemistry.

5.0 Summary

The **Levich Equation** models the diffusion and solution flow conditions around a RDE (RDE). It is named after Veniamin Grigorievich Levich who first developed an RDE as a tool for electrochemical research. It can be used to predict the current observed at an RDE, in particular, the Levich equation gives the height of the sigmoidal wave observed in rotating disk voltammetry. The sigmoidal wave height is often called the Levich current.

The Levichequation can be written as:

$$i_{L,C} = 0.620nF(D)^{\frac{2}{3}}v^{\frac{-1}{6}}C\omega^{\frac{1}{2}} \qquad 3.14$$

whereI_L is the Levich current (A), *n* is the number of electron transferred in the half reaction (mol^{-1}), F is the Faraday constant (C/mol), A is the electrode area (cm^2), *D* is the diffusion coefficient (cm^2/s), *w* is the angular rotation rate of the electrode (rad/s), *v* is the kinematic viscosity (cm^2/s) and C is the analyte concentration (mol/cm^3)

6.0 Tutor-marked assignment

1. Define the term, flux as it relate to mass transport in electrochemistry. In what way does the flux relate to Fick's first law of diffusion?
2. What are the three major aspects of mass transport in electrochemistry?. Write a general equation to show how these three aspect are related to mass transport
3. What is the significance of Stokes' law in mass transport? Use suitable mathematical derivation to support your answer
4. Write the general form of the Levich equation. What is the significance of the equation in electrochemistry?

7.0 References/Further reading

Atkins, P. and De Paula, J. (2010). Atkins'Physical Chemistry.Ninth Edition.Oxford University Press. UK.

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry.5th Edition.Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

Unit 2

1.0 Introduction

The first scientist who discovered the use of the DME in electrolysis is Jaroslave Heyrovsky in 1922 and received the Nobel Prize in Chemistry in 1959. Polarography was the first of the voltammetric techniques to gain prominence. Certainly the most popular constant potential method is d.c. polarography at a dropping mercury electrode (DME).

Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. The electrode whose potential is varied is called the indicator electrode voltammetric indicator electrodes may be made from quite a large number of materials say for instance mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or is motion and the solutions in which these are used may be stationary or quiet.

2.0 Objectives

At the end of this model, students should be able to:

- Describe polarography and its principles
- Identify the physical problems that can be handled using polarography
- Derive the Ilkovic equation and explain the significant of basic terms in the equation
- Sketch a plot for a typical pattern of a polarogram
- Solve some problems related to polarography

3.0 Main content

3.1 Theory and principles of polarography

Polarography is the study of the electrolysis of solutions of electro-oxidizable and or electro-reducible substances between a dropping mercury electrode (DME) and some reference electrode (RE). The potential between these electrodes is varied and the consequent change in the flow of current is measured. On plotting the changes in current flow versus the potential variation, an i-E curve is obtained known as polarogram (Fig.3.3).

The slowly increasing current at the foot of the wave is known as the residual current. This current is non faradaic in nature. The diffusion current i_d is, as shown, the distance between the limiting diffusion plateau and the residual current. The potential at the midpoint of the wave, where the current is exactly half its limiting value, is known as the half-wave potential $E^{1/2}$ and its quantity is characteristic of a particular species under fixed experimental conditions. Thus $E^{1/2}$ value serves as finger-print for the species undergoing redox reaction.

In addition, the limiting current is proportional to concentration of the species being reduced or oxidized and thus serves for quantitative analyses. Over the diffusion current plateau region the DME is behaving as a completely polarized electrode since it adopts any applied potential to it with no change in current flow. It is significant to note that polarization always results from slow stage in the overall electrode process. The slow stage here is the diffusion process which occurs very much slower than the electron transfer. This type of polarization is known as concentration polarization and the DME is said to be concentration polarized. At potentials corresponding to the rising part of the wave the electrode is depolarized since here the current flow is strongly dependent on the applied potential. At this stage it is important to emphasize that in any electrolysis two types of processes are encountered.

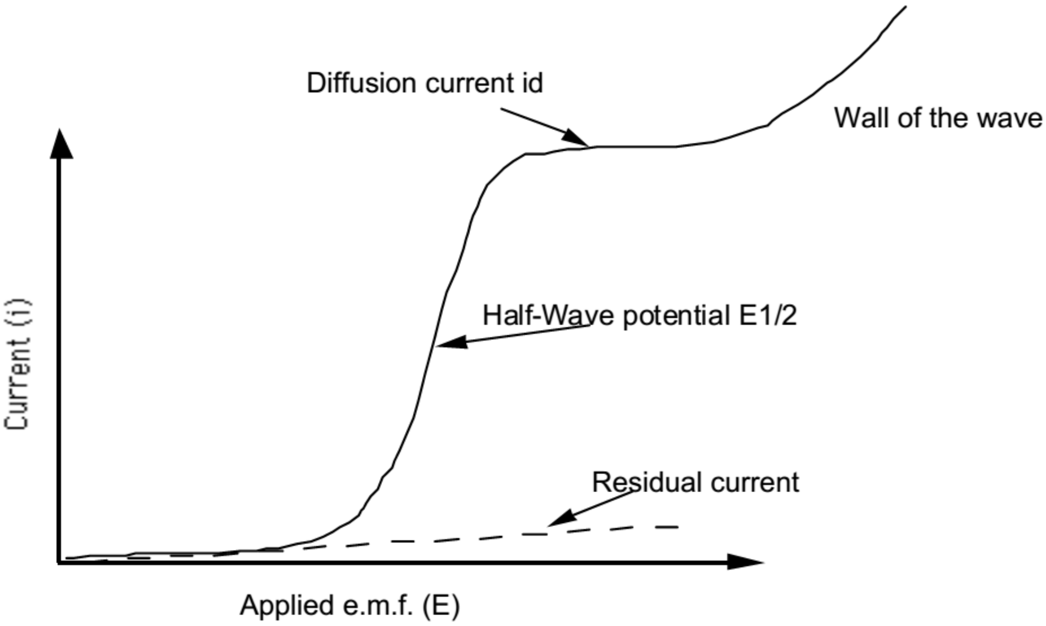

Fig. 3.3: Typical pattern of a polarogram

i. Mass transfer process which brings the electroactive material to the electrode surface
ii. Electrochemical process which involves the act of electron transfer between the surface of electrode and the electroactive species.

As stated before, mass transfer is usually achieved through migration, diffusion and convection. Migration is an electric field effect and depends upon the charge on the species, concentration and mobility in a field of force. Diffusion depends upon differences in concentration between species at the surface of the electrode and in the bulk of solution. Finally convection arises from any mechanical or thermal disturbance in the solution. For a redox process to occur it is essential that electrons pass between the electrode and the species in solution. However, before electron transfer can be effective, processes such as adsorption and rearrangement of electronic configuration within the species must occur in order to give a suitable form for the electron exchange. After the electron exchange, a primary product is formed which re-undergoes an electronic rearrangement, desorption and may suffer further side reactions to form the final product. These electrolytic processes may be reversible or irreversible in nature depending on the activation energy values.

3.2 Diffusion Current, i_d

According to Fick's first law of diffusion, the rate of diffusion is proportional to the concentration gradient. Since diffusion in polarography is the rate determining step, the rate of diffusion can be equated to the rate of electrode reaction. Hence the rate of the electrode reaction is proportional to the concentration gradient. That is,

$$Rate\ of\ diffusion\ \alpha\ \left(\frac{dC}{dx}\right)(x = 0) \qquad 3.15$$

Equation 3.15 can also be written as follows,

$$\frac{i}{nFA}\quad \alpha\ \left(\frac{dC}{dx}\right)(x = 0) \qquad 3.16$$

Simplification of equation 3.16 yields equation 3.17

$$i\ = nFAD\left(\frac{dC}{dx}\right)(x = 0) \qquad 3.17$$

where A is the surface area of a plane electrode, across which a current i passes due to the impressed emf , n is the number of electrons, F is the Faraday, D is the diffusion coefficient in $cm^2/sec.$, C is the concentration , x = 0 means at the electrode surface.

As stated before, under polarization, if the concentration of the active specie on the surface and bulk are C_S and C_B, then the concentration gradient is, $\frac{dC}{dx} = \frac{(C_B - C_S)}{\delta}$ and by substitution into equation 3.17, equation 3.18 is obtained,

$$i = nFAD\left(\frac{C_B - C_S}{\delta}\right) \qquad 3.18$$

Also, as stated earlier, maximum current will flow in the cell when $C_S = 0$ and the current that flows under this condition is called limiting current (i_L), which is equal to diffusion current in this case, hence,

$$i_d\ = nFAD\left(\frac{C_B}{\delta}\right) \qquad 3.19$$

Where i_d is the maximum limiting current. Fick's first law is limited only for the cases where the diffusion layer is of constant thickness and where the conditions are stationary. In other cases when the diffusion layer thickness alters with time and concentration is varying with both time and distance, Fick's second law is most appropriate (equation 3.20):

$$\frac{dC}{dt}\ =\ D\left(\frac{d^2C}{dx^2}\right) \qquad 3.20$$

Fick's second law (equation 3.20) can only be solved mathematically by Laplace integral transform resulting in the Cottrell equation. This equation reveals that i_t decreases with time due to a broadening of the diffusion layer and a decrease in the diffusion rate. Equation 3.20 is the backbone of the Ilkovic equation. Generally, i_t can be written as follows,

$$i_t = nFAD^{\frac{1}{2}}C_B\pi^{\frac{1}{2}}t^{\frac{1}{2}} \qquad 3.21$$

In order to obtain the Ilkovic equation, we assume that the drop is spherical and that the mercury flow rate is uniform, that is, that the drop volume increases linearly with time. Which implies that its $A = 4\pi r^2$, $V = (4/3)\pi r^3$, $d = W/V$ and $V = W/V = 10^{-3}mt/d$. Combining these functions, we have the values for the radius (equation 3.22):

$$r = \left(\frac{[3 \times 10^{-3}mt]}{[4d]}\right)^{\frac{1}{3}} \qquad 3.22$$

If we replace value of r in equation 27 into the formula for calculating area (i.e$A = 4\pi r^2$):

$$A = \left(\frac{6 \times 10^{-3}\pi^{\frac{1}{2}}mt}{d}\right)^{\frac{2}{3}} \qquad 3.23$$

Substituting for A in equation 4.7 (using equation 3.23), we obtained equation 3.24, which simplifies to equation 3.25

$$i_t = \left\{\left(nFC_BD^{\frac{1}{2}}t^{\frac{1}{6}}\right)/\pi^{\frac{1}{6}}\right\}\{(6 \times 10^{-3}m)/d\}^{\frac{2}{3}}\left(\frac{7}{3}\right)^{1/2} \qquad 3.24$$

$$i_d = 708nD^{\frac{1}{2}}t^{\frac{1}{6}}m^{\frac{2}{3}}C_B \qquad 3.25$$

where V is the volume in cm^3, W is the weight of the drop in g, m is the rate of Hg flow in mg/sec. , d is the density g/cm^3, (7 /3)2/3 is introduced to account for the fact that the drop is continually expanding. Equation 38 is called the Ilkovic equation where i_d is expressed in µA, C_B in mM per liter and t in seconds. The equation is a linear equation of the form, $i_d = KC_B$. This linear relation is the basis of quantitative analyses (calibration curve) in polarography.

3.3 The half-wave potential and its significance

The most important constant in polarography is the half-wave potential. Chemical, thermodynamic and structural information may be obtained from the measurements of the half-wave potentials of reversible and irreversible waves under varying experimental conditions.

The manner in which the current is affected by electrode potential on the rising part of the wave is to be noted. On the plateau, electron transfer is so fast that the ions or molecules of the electroactive substances are reduced or oxidized as rapidly as they arrive or are formed at the electrode surface. As the potential moves from the plateau of the wave towards its foot, the rate of the electron-transfer process decreases and the reduction or oxidation becomes less and less complete.
It is convenient to divide electrode reactions into two extreme classes:

(i) Reversible reactions, and
(ii) Irreversible reactions.

The reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions the variation of current with potential reflects the changing position of the equilibrium and is described by Nernst equation. The other extreme is that of totally irreversible reactions, which are so slow that they proceed only by a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron-transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between current and potential. The polarographic data serve to elucidate the kinetics of the rate determining step in totally irreversible processes.

3.4 Factors affecting the half-wave Potentials

1. The temperature coefficient of the half-wave potential is mostly between –2 and +2 mv/degree. For a reversible wave it may be either positive or negative. For an irreversible wave it is usually positive and may exceed several millivolts per degree.

2. The half wave potential is almost always independent of the concentration of the electroactive species (i.e., of the diffusion current) after proper correction is applied for the iR drop. However, the half-wave potential of a reversible wave does not vary with concentration if a solid product is termed, or more generally, whenever the number of the ions or molecules of the product of variable activity differ from the number of ions or molecules of reactant of variable activity in the equation for the half-reaction. Such variations can be described only by thermodynamic equations. The half-wave potential of an irreversible wave may

also vary with concentration of the reaction mechanism involving some rate governing step that is not the first- or pseudo-first order. When it does vary, it most often becomes more negative as the concentration increases.

3. The half-wave potential of a reversible wave is nearly independent of the capillary characteristics, i.e., mass (m) and time (t). When the diffusion current obeys the Koutocky equation and when the diffusion coefficient of the oxidized and reduced species differ a small dependence of the half-wave potential on $^{t1/6}$ and $m^{1/3}$ can be predicted. Changes in m, t and the concentration of the electroactive species can produce apparent variations of the half-wave potential unless both are corrected. The iR drop always produces an apparent shift of the half-wave potential toward more negative values for the cathodic waves and toward more positive values for anodic waves and the shift is proportional to the limiting current.

4. Changes in the nature and concentration of supporting electrolyte may affect the half-wave potential in many ways. For reversible waves the effect is due to complex formation.

5. When a complex metal ion is reversibly reduced to a metal soluble in mercury, its half-wave potential is always more negative than that for the reversible reduction of the corresponding simple or aquo-complex ion. Complex formation may cause the half-wave potential in the irreversible reduction of a metal ion to become either more negative or more positive. This depends on the nature of the ligand used.

4.0 Conclusion

Polarography is a subclass of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which is useful for their wide cathodic ranges and renewable surfaces.

Polarography is a voltammetric measurement whose response is determined by combined diffusion/convection mass transport. Simple principle of polarography is the study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable, the former formed by mercury regularly dropping from a capillary tube. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential response of a polarographic experiment has the typical sigmoidal shape.

5.0 Summary

Polarography is based on the principle of mass transport and it is a method that has been widely used in laboratory and industrial analysis although it has some limitation, it has found wider application in analysing for the underlisted parameters in pharmaceutical products

- Dissolved oxygen and peroxides.
- Trace metals and metal-containing drugs.
- Antiseptics and insecticides.
- Vitamins.
- Hormones.
- Antibiotics.
- Alkaloids.
- Blood serum and cancer diagnosis.

Therefore, the study of polarography is sustained by its wider applications in industries.

6.0 Tutor mark assignment

1. What is the importance of mass transport in polarography?

2. Sketch a typical nature of a polarogram and explain important parameters that can be obtained from such plot

3. What is the significant of half wave potential in polarography?

4. What is the importance of diffusion current in polarography? Write the Ilkovic equation and explain how the diffusion current connects with measurable quantities. Finally, how can this equation be applied for analytical purpose?

7.0 References/Further reading

Atkins, P. and De Paula, J. (2010). Atkins'Physical Chemistry.Ninth Edition.Oxford University Press. UK.

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry.5th Edition.Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

Bard, Allen J.; Parsons, Roger; and Jordan, Joseph, eds. (1985).*Standard Potentials in Aqueous Solutions*.New York: Marcel Dekker.

Bard, Allen J., and Faulkner, Larry R. (2000).*Electrochemical Methods: Fundamentals and Applications*. New York: Wiley.

Bockris, J. M., and Reddy, A. K. N. (1998).*Modern Electrochemistry*.New York: Plenum.

Oldham, Keith B., and Myland, Janice C. (1994).*Fundamentals of Electrochemical Science*.New York: Academic Press.

Rieger, Philip H. (1994). *Electrochemistry,* 2nd edition. New York: Chapman and Hall.

MODULE 4:

Unit 1: Electronics in electrochemistry

1.0 Introduction

2.0 Objectives

3.0 Main text

4.0 Conclusion

5.0 Summary

6.0 Reference/Further reading

1.0 Introduction

Electronics is the science of how to control the electrical energy, in which the electrons have a fundamental role. Electronics deals with electrical circuits that involve active electrical components such as vacuum tubes, transistors, diodes and integrated circuits, and associated passive electrical components and interconnection technologies. Commonly, electronic devices contain circuits consisting primarily or exclusively of active semiconductors supplemented with passive elements; such a circuit is described as an electronic circuits. Most electrochemical instruments rely on the measuring of some physical process for example amount of current, voltage, resistant, capacitance, etc. Generally, an electrochemical instrument will has a signal as the input, a transducer, signal processor and read out system as the functional element (Fig. 4.1)

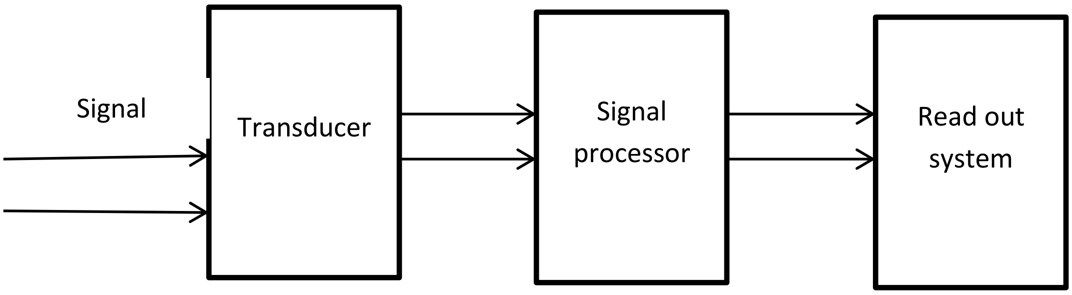

Fig. 4.1: Block diagram of a measuring instrument

Input signal enters the instrument through the transducer. The transducer produces an internal signal which has to be amplified before it can be read from the read out system. A signal represents some form of information or a means of carrying the information. A transducer is a functional element of a instrument which receives the input signal and produces an output signal (internal signal) that has to pass through a signal processor. All transducers work through some form of physical properties.

2.0 Objectives

At the end of the Unit, students should be able to:

- Identify the basic elements needed in electrochemical instruments
- Highlight the importance of circuits in electrochemistry
- Highlight the functions of transducer and detector in electrochemical instruments
- Examine some electrochemical cells and the mechanism of flow of electrons within the cell

3.0 Main content

3.1 Transducer and detector

A transducer is used to convert energy or information (input signal) from one form to another. The pH electrode for example is a transducer that responds to a change in the potential difference between a liquid in a sealed glass and the sample solution to be measured. A pH electrode consists of a glass bulb that contains 0.1 M HCl saturated with AgCl. However, for analytical purpose, the pH meter has to be used in conjunction with a reference electrode. The common type of a reference electrode is the colomel electrode. The pH electrode is sensitive to pH change. It is a thin membrane of special glass, which separates the solution being tested from a saturated solution of AgCl. Most pH meters/electrodes combine the features of the pH electrode and that of the reference electrode into a single electrode called combination electrode.

When the glass electrode is inserted into a solution for analytical purpose, a voltage difference is generated between the two surfaces of the glass membrane and the magnitude of the generated voltage depends on the pH of the solution being tested. Theoretical voltage output from a pH meter can be calculated from the Nernst equation. The chemical equation that is significant in pH study is expressed in equation 4.1

$$H^+ \quad + \quad e^- \quad = \quad ½\,H_2 \qquad\qquad 4.1$$

Applying the Nernst equation to equation 31, we have equations 4.2 and 4.3:

$$E_H \;=\; E^0 \;-\; \frac{2.303RT}{F} loga_{H^+}^{+} \qquad\qquad 4.2$$

$$E_H = E^0 - \frac{2.303RT}{F} pH \qquad 4.3$$

Equation 33 can be simplified to equation 5.4

$$E_v - E_0 = -0.198T(pH - 7.0) \qquad 4.4$$

where E_V is the voltage being measured in millivolt and T is the temperature of the solution in Kelvin. The value of E_0 depends on the particular electrode being used and is almost constant for a given electrode.

Other types of electrode that operates in similar principles are ion selective electrodes (electrochemical transducers) which are sensitive to a particular ion. Generally, in all electrochemical instruments, the output signal determined the type of signal processor that is required. The sensitivity of a transducer is defined as the ratio of the magnitude of the output signal to the magnitude of the input signal. Its selectivity is also defined as the ratio of its sensitivity to the input signal (to be measured) to the sensitivity to other input signal.

3.2 Electrochemical circuits

Electrochemistry can be defined as the branch of chemistry that deals with chemical reactions which take place at the interface of an electrode, usually a solid metal or a semiconductor, and an ionic conductor (the electrolyte). These reactions therefore involve the movement of electric charges between the electrodes and the electrolyte (or ionic species in a solution). Hence, electrochemistry deals with the interaction between electrical energy and chemical change.

A chemical reaction caused by an externally supplied current, such as electrolysis, or if an electrical current is produced by a spontaneous chemical reaction as in a battery, , it is called an electrochemical reaction. Chemical reactions where electrons are transferred directly between molecules and ions are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

From the above, it can be seen that electrochemical reactions involves the interaction of charged ions or electrons. They must be a power source, electrolyte and electrodes. Other circuit elements such as galvanometer, voltammeter and others, may be useful. Hence, the arrangement of the various components that are needed to complete an electrochemical cell can be done by using electrical circuit. This section considers some electrical circuit in some electrochemical instruments.

3.2.1 Polarization circuit

Fig. 4.2 shows the components needed for polarization study, using a potentiostat. It can be seen from the diagram that voltmeter, ammeter, electrodes (reference electrode, working electrode and counter electrodes) are needed.

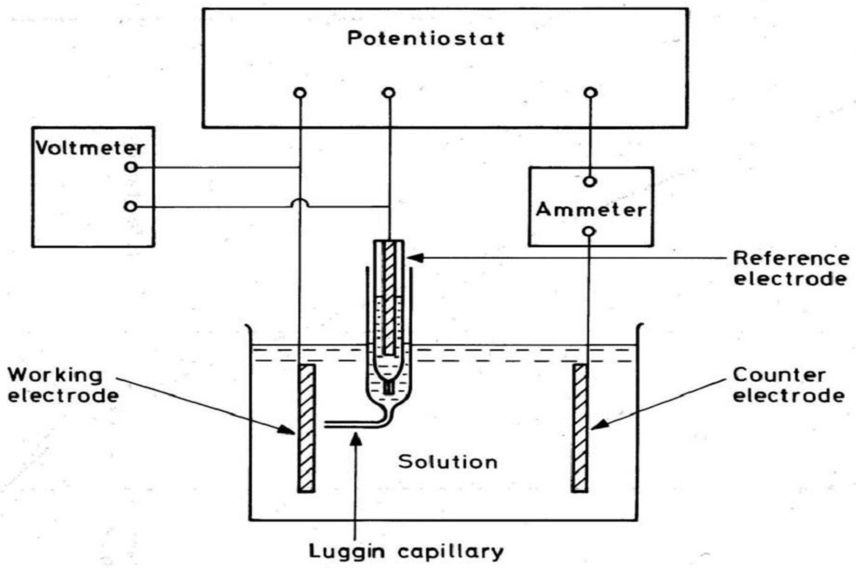

Fig. 4.1: Block diagram showing components for polarization study using a potentiostat

In Fig. 4.2, the arrangement show in in Fig. 4.1 is presented**.**

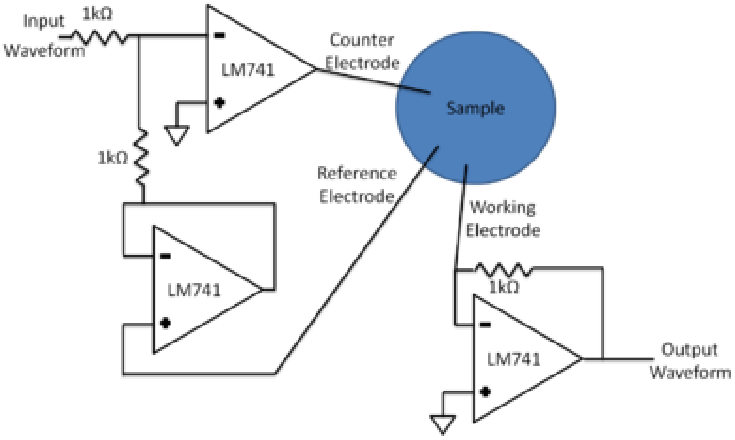

Fig. 4.2: Circuit diagram for potentiostat
(Source: http://2011.igem.org/Team:Calgary/Project/Reporter/Prototype)

3.2.2 Circuit for measuring emf

In Fig. 4.3, a circuit for measuring emf is presented, where E is the power source, E_S is the standard or known cell and E_X is the unknown cell. EMF is the potential when the cell is no producing any current. It is sometime called the zero current or open circuit potential. In order to measure the emf of a cell, the potentiometer slide wire is adjusted until there is no current through the galvanometer (G) When the slide is in position 2, then $R = R_S$. The process is repeated for position 1, where $R = R_X$. From the above, $E_X = I_0R_X$ and $E_S = I_0R_S$. At equilibrium, $E_X = E_S$ and $E_X = (R_X/R_S)$ ES.

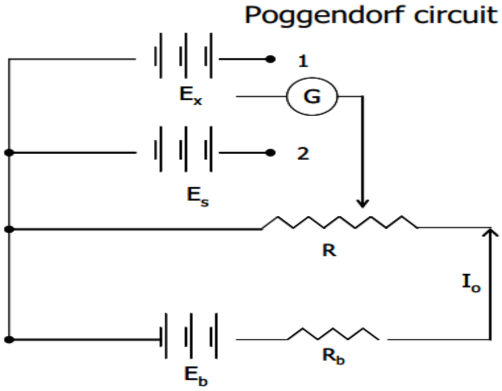

Fig.4.3 Electric circuit for measuring emf or pzc of a cell

3.2.3 Electrochemical impedance spectroscopy

A Randles circuit is an equivalent electrical circuit that consists of an active electrolyte resistance R_s in series with the parallel combination of the double-layer capacitance C_{dl} and an impedance of a faradaic reaction. It is commonly used in electrochemical impedance spectroscopy (EIS) for interpretation of impedance spectra, often with a constant phase element (CPE) instead of the double layer capacity (C_{dl}).

Figure 4.4 shows the equivalent circuit initially proposed by John Edward Brough Randles for modeling of interfacial electrochemical reactions in presence of semi-infinite linear diffusion of electroactive particles to flat electrodes. In this model, the impedance of a faradaic reaction consists of an active charge transfer resistance R_{ct} and a specific electrochemical element of diffusion W, which is also called Warburg element ($Z_W = A_W/(j\omega)^{0.5}$, where A_W is Warburg coefficient, j – imaginary unit, ω – angular frequency).

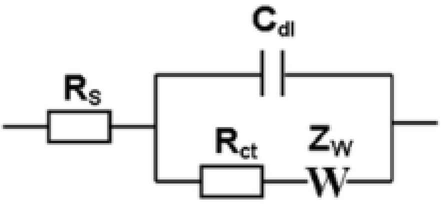

Fig. 4.4: Randles circuit schematic.

4.0 Conclusion

Electronics is an essential aspect of electrochemistry and its importance can not be over emphasized. All electrochemical instruments are designed to take measurements which operate through signals (input or output signals. The essential elements of electrochemical analytical instruments have been presented in this unit. It can therefore be concluded that electronics and instrumentations are relevant in electrochemistry.

5.0 Summary

Electrons has a fundamental role in electrochemistry, therefore the study of electronics under this course is essential. In view of this, electrochemistry deals with electrical circuits that involve active electrical components such as vacuum tubes, transistors, diodes and integrated circuits, and associated passive electrical components and interconnection technologies.

6.0 Tutor-marked assignments

1. Identify one electrochemical instrument and answer the following questions

i. What are the major functional elements in the instrument?

ii. What is the input and expected output signal in the instrument?

iii. What is type of read out system in the instrument?

iv. How will you define the sensitivity and selectivity of the instrument?

7.0 References/Further readings

Bard, Allen J.; Parsons, Roger; and Jordan, Joseph, eds. (1985).*Standard Potentials in Aqueous Solutions.*New York: Marcel Dekker.

Bard, Allen J., and Faulkner, Larry R. (2000).*Electrochemical Methods: Fundamentals and Applications.* New York: Wiley.

Bockris, J. M., and Reddy, A. K. N. (1998).*Modern Electrochemistry*.New York: Plenum.

Oldham, Keith B., and Myland, Janice C. (1994).*Fundamentals of Electrochemical Science*.New York: Academic Press.

Rieger, Philip H. (1994). *Electrochemistry*, 2nd edition. New York: Chapman and Hall.