Sensor Innovations Based on Modified Carbon Electrodes

PhD Thesis

Norahim Bin Ibrahim

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Summary

This thesis describes experimental work on electrochemical sensing mechanisms. Chapter 1 and Chapter 2 provide an introduction to electrochemical and surface science techniques as well as nano-carbon materials which are of interest in electroanalysis and sensing.

Chapter 3 and Chapter 4 focus on electrochemical processes at liquid | liquid | electrode triple phase boundary systems. In Chapter 3 the electrochemical behaviour of CoPc (cobalt phthalocyanine) dissolved into an organic water –insoluble liquid and deposited as microdroplets on a graphite electrode is studied. Both cation and anion transfer are observed at the liquid | liquid phase boundary. Chapter 4 describes redox processes of a highly hydrophobic anthraquinone derivative where preferential transfer of protons and pH sensitivity are observed. Both systems, CoPc and anthraquinone derivative, are investigated towards CO_2 sensitivity.

In Chapter 3 and 4 graphite electrodes are employed, but in Chapter 5 graphitic carbon nanoaprticles are employed with a surface functionalisation to provide binding capability to DNA fragments. Layer-by-layer deposition of DNA-carbon nanoparticle composite film electrodes is demonstrated and the electrochemical properties of the films are investigated. A novel type of DNA hybridisation sensing mechanism based on a nano-gap generator – collector electrode system is proposed.

Chapters 6 and 7 are dedicated to gas sensing with a novel electrochemical system based on ionomer spheres in contact to the working electrode. In Chapter 6 Dowex ionomer particles are impregnated with carbon nanoparticles which are functionalised with DOPA to provide redox activity and Faradaic current responses. The effect of ionomer type and gas composition is studied. In Chapter 7 Prussian blue nanoparticles are immobilised onto the ionomer particle surface to provide a sensing system with peroxide sensitivity.

Overall, this thesis contributes to sensing of bio-molecules and of gases. By introducing new types of interfaces (triple phase boundary, ionomer contacts, carbon nanoparticle redox systems) it is shown that sensitivity and selectivity can be tailored. In future these types of sensor prototypes could be further developed for specific applications.

List of Abbreviations

AA	ascorbic acid
AC	alternating current
AFM	Atomic Force Microscopy
bppg	basal plane pyrolitic graphite
CMWNT	carbon multiwalled nanotube
CNF	carbon nanofiber
CNP	carbon nanoparticle
CNT	carbon nanotube
CR-GO	chemical reduced graphene oxide
CRG	chemically reduced graphene
CV	cyclic voltammetry
CVD	chemical vapor deposition
DC	direct current
DNA	Di nucleic acid
DPV	Differential Pulse Voltammetry
EDS	Energy Dispersed X-Ray Spectrometer
EMF	Electromotive Force
FEGSEM	Field Emission Gun Scanning Electron Microscopy
GC	glassy carbon
GO	graphene oxide
GOD	glucose oxidase
HOMO	Highest Occupied Molecular Orbital
IHP	Inner Helmholtz Layer
ITO	Indium induced Titanium Oxide
IC	integrated circuit
LUMO	Lowest Unoocupied Molecular Orbital
MG	methylene green
MGNFs	multilayer graphene nanoflake films
MOD	Metal Organic Deposition
NP	nanoparticle
OHP	Outer Helmholtz Layer
PECVD	plasma enhanced chemical vapor deposition
RF	radio frequency
SLG	single layer graphene
SHE	Standard Hydrogen Electrode
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SPM	Scanning Probe Microscope
SWNT	single wall nanotube
TCVD	thermal chemical vapor deposition

List of Symbols

Symbol	Quantity	Units
A	electrode surface area	cm^2
A	frequency factor	-
C	capacitance	$F\ m^{-2}$
c	concentration	$mol\ cm^{-3}$
D	Diffusion coefficient	$cm^2\ s^{-1}$
E	potential	V
E_{eqm}	equilibrium potential	V
E_{pz}	potential of zero charge	V
F	Faraday constant	$C\ mol^{-1}$
ΔG	Gibbs free energy	$kJ\ mol^{-1}$
ΔG^*_{red}	Gibbs free energy of reduction	$kJ\ mol^{-1}$
h	Planck's constant	J s
i_p	peak current	A
j	flux of reactant	$mol\ cm^{-2}\ s^{-1}$
j_{cap}	capacitive current density	$A\ m^{-2}$
k	wavenumber	-
k^0	standard electrochemical rate constant	$cm\ s^{-1}$
R	gas constant	$Jmol\ K^{-1}$
T	temperature	K
ρ	charge	C
Φ	potential	V
η	potential difference / overpotential	V
α	charge transfer coefficient	-
λ	wavelength	m
ν	frequency	-
ν	scan rate	$mV\ s^{-1}$

Chapter 1

Introduction to Electrochemical Methods
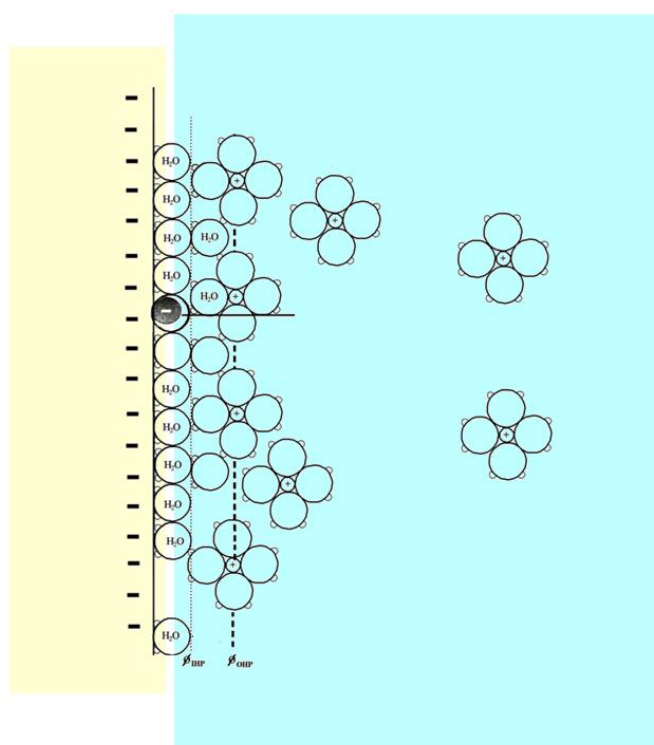
This chapter provides an introduction into experimental methods and theory for electrochemical methods and surface analysis techniques.

Contents

1.1 Polarization of Interfaces

1.1.1 Interfacial Region

Electron transfer is an event in a molecular scale where a negatively charged entity passes through between an electrode and a species in solution. The reason for electron transfer to occur is the potential gradient present at the electrode surface which results from the difference in potential values when two different materials or phases come in contact with each other; between a solid electrode and the electrolyte solution. For example, the potential difference between a local electrode and the adjacent solution may be 1 V, measured over a gap between 1 nm, then the potential gradient shall be of the order of 10^9 V m^{-1} [1]. When studying the rate of electron transfer, a considerable thought on the potential gradient at the interfacial region is of vital importance.

Whenever a potential is applied to the electrode surface, a charging characteristics involving the electrostatic effect is observed. Ions and dipoles with opposite charges are most likely attracted to the electrode surface. This eventually results in the formation of "electrical double layer" [2]. The movement of ions to the adjacent of electrode surface causes changes in the potential field and this factor is indispensable when considering the kinetics of electron transfer.

1.1.2 The Electrical Double Layer

Supposed that there shall be no electron transfer occurring at the interface of the elecrode and the solution. In other words, no chemical changes take place and so no faradaic current passes. Such an electrode is called ideally polarized electrode as there is no electrode reactions can occur within a certain range of potential values [3]. Ideally polarized electrode behaves like a capacitor and only capacitive current flows upon a change of potential. A lot of electrodes posses this kind of characteristic but only within an electrode potential range called the double-layer range.

As mentioned previously, if a potential is applied to an electrode immersed in a solution, the electrode surface will become charged. The amount of charge on the electrode surface is proportional to the electrode material, the electrolyte and potential applied. If the potential applied is negative, then the electron will flow into the surface eventually turning the surface to be negatively charged. In an opposite way, if the applied potential is positive, electron will move out of the surface, gradually results in it being positively charged. Accompanying this phenomenon is the rational that for every electrode/electrolyte combination, there must be a potential whereby the surface shall be neutrally charged. This potential is called zero charge, E_{pzc}. The surface charge on the electrode is in fact balanced by the movement of counter ions from the bulk solution.

Extending the argument above, whenever the electrode potential is negative to E_{pzc}, its surface will become negative. Balancing this, the cations and dipoles such as water molecules begin to be attracted to the electrode surface. Similarly, if the potential applied is positive relative to the E_{pzc}, the electrode surface becomes positively

charged thus inviting anions and dipoles to its adjacent. It shall be noted that in this case, the orientation of the dipoles will be reversed. Either way, there shall be an organized layer consists of cations or anions formed very close to the electrode surface resulting from the potential changes. It shall also be stated that the higher value the applied potential is, the stronger the electrostatic forces produced. As a matter of fact, competition for sites on the electrode surface does exist between the ions and water dipoles in order to form a well organized double layer. An example of the formation of double layer is depicted in Figure 1 [1].

Thus when the potential of an electrode in an aqueous electrolyte is negative to E_{pzc}, its surface will be negatively charged and both cations and dipoles, particularly water molecules, will be attracted to the surface. Moreover, the more negative the applied potential, the stronger are the electrostatic forces leading to the formation of an organized layer of cations adjacent to the electrode surface. Conversely, positive to E_{pzc}, the electrode surface will be positively charged and it is anions and dipoles which are attracted (note, the orientation of the dipole will be reversed). In practice, there will be competition between the ions and water dipoles for sites on the surface and the electrostatic forces leading to a totally organized structure are opposed by the thermal motion of the ions. Figure 1.1 shows the generally accepted model for the interfacial region when $E < E_{pzc}$ and which includes the following features.

1. IHP Inner Helmholtz Layer
2. OHP Outer Helmholtz Layer
3. Adsorptive anions
4. Solvated cations
5. Diffuse layer
6. Solvent molecule.
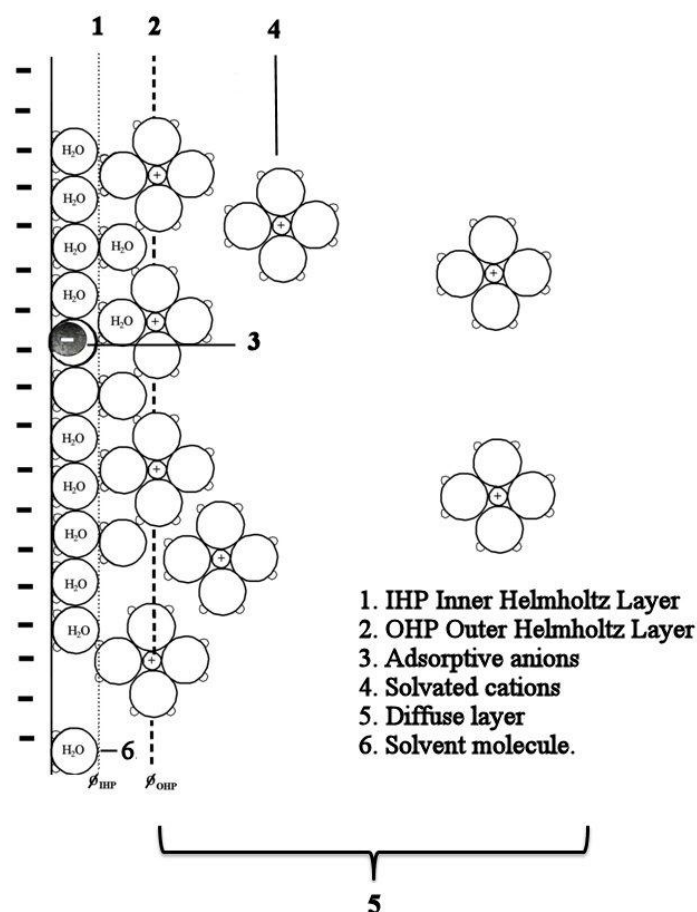
Figure 1.1 Model of electrical double layer at the interfacial region at the electrode surface for potentials negative to the potential of zero charge [1]**.**

1.1.3 Charging Currents

It was stated that any change in the potential of an electrode is the driving force of change in the charge on the metal side of the electrode surface. Coupled to this, ions and dipoles reorganization will also occur in the double layer on the solution side. Changing the potential of the electrode means that there will be electron flowing into or out of the electrode. In practice, these electrons will eventually pass out through the external circuit and virtually seen as current and called "charging current".

Charging current is additional to the Faradaic current, which comes from the reactive species in the cell. Its presence is always regarded as "noise" as it complicates the signals produced by the reaction desired in the particular experiment setup. It shall be emphasized that the effect of charging current is only a minor problem for short timescale experiments as reorganization of double layer according to the potential change occurs very fast and, once the new structure has been formed the charging current effect can be totally neglected [1].

For example, in linear potential sweep or cyclic voltammetric experiment, the charging current may be estimated from equation 1. A typical value of capacitance is 0.2 F m^{-2} so that at scan rates of 0.1 and 100 V s^{-1} the observed capacitive current density $j_{cap} = 0.02$ and 20 A m^{-2}, respectively.

$$j_{cap} = C \times v \qquad\qquad (1.1)$$

The current density is given by equation 1.1. Here C is the capacitance and v is the potential scan rate. The capacitive current at high scan rate commonly is of the same order of magnitude or higher compared to the Faradaic current for a diffusion controlled reaction.

1.2.   Electrode Kinetics

An example of a reduction for a cation can be taken from Figure 1.1. In order for the

electron transfer to occur at a potential negative to E_{pzc}, the cation must be as close as

possible to the electrode. Let's say it has to sit on the plane of closest approach. It is

important to note that whether or not the electron transfer occurs at the interface, the

structure and properties of the double layer remains the same. Also, it shall be

emphasized that the resulting structure as well as the behaviour of the double layer

originates from the electrostatic effect, not chemical. For these reasons, in a system

where the electroactive species exist in a large excess of inert electrolyte, it will solely

the ions which will determine the characteristics of the double layer. In practice, the

effect of double layer is always minimized by using inert electrolyte.

To understand the the electrode kinetics, consider a reduction process for

hexacyanoferrate(III) to hexacyanoferrate(II) in a solution using an electrode surface

area of A cm^2, with a suitable negative potential applied [4].

$$Fe(III)(CN)_6^{3-}(aq) + e^- \leftrightarrow Fe(II)(CN)_6^{4-}(aq) \tag{1.2}$$
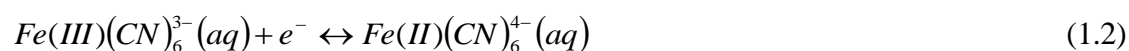
In order for electron transfer to occur between two phases (metal/solution), the

electroative species, $Fe(CN)_6^{3-}$ has to be as close as 10-20 Å from the electrode

surface. Reduction of the $Fe(CN)_6^{3-}$ anion is only possible if it diffuses within this

vicinity, from bulk solution to electrode surface.

The movement of electron in return creates the current which flows through the electrode and external circuit. The relationship between the current generated from the electron transfer can be shown as below.

$$i = FAj \qquad\qquad (1.3)$$

F = Faraday constant

A = electrode surface area

j = flux of reactant undergoing electrolysis
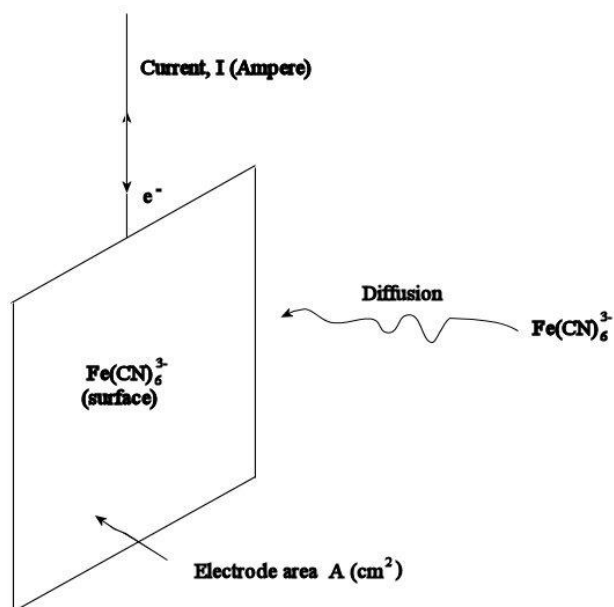
Figure 1.2 Diffusion process of $Fe(CN)_6^{3-}$ to the electrode from bulk to solution [5].

Here, the flux can be best described as the rate of the heterogeneous reaction at the electrode interface. The unit is mol cm^{-2} s^{-1}, and is measured the same way for homogeneous chemical reaction which can be shown as below.

$$j = d[reac\tan t]/dt \qquad\qquad (1.4)$$

The flux for a heterogenous reaction at the electrode-solution interface can be written as:

$$j = k(n)[reac\tan t]_n^0 \qquad\qquad (1.5)$$

Where n is the rate order of the reactant, k(n) is a nth order rate constant and the subscript represents the concentration of reactant at the electrode surface, which implies the minimum electron tunnelling distance. As far as the equation 1.5 is concerned, there are three main considerations that shall be emphasized.
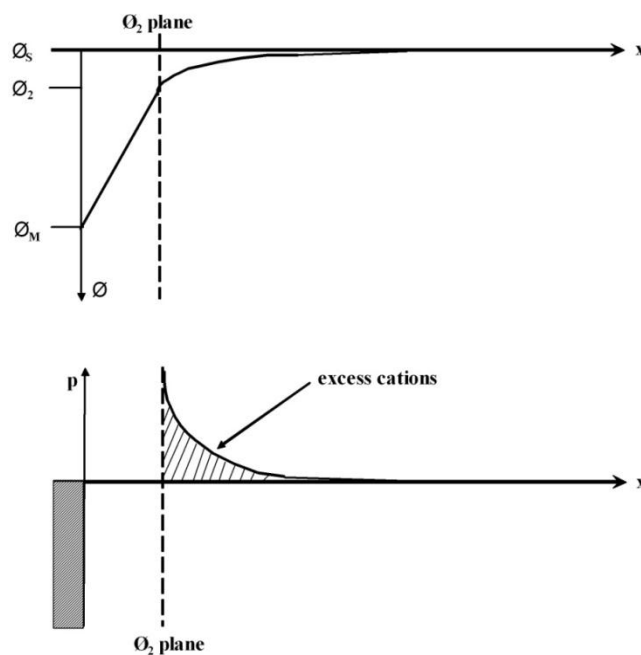
Figure 1.3 Qualitative representation of the charge, ρ, and potential, Ø, as a function of distance from the surface resulting from the model of Figure 1.1 [1].

Firstly, it is very significant to point here that for a first order heterogeneous reaction, n is always equal to 1, and this makes the unit for k(1) are in cm s^{-1}. In contrast to the first order homogeneous reaction, which differs only in s^{-1} in dimensions. Secondly, the concentration of the electroactive species where the electron transfer occurs, the ψ –plane, is not the same as in bulk solution. The concentration of at the ψ-plane may be lower, the same, or higher than that of the bulk solution depending whether the electroactive species are cations or anions, or whether the applied potential is positive or negative to the E_{pzc}. Thirdly, it goes without telling that temperature and pressure are two important parameters in determining the heterogeneous rate constant as well as in homogeneous reactions, but the most critical point of all for interfacial reactions is the applied potential. The driving force for electron transfer relies on the potential difference between the electrode and the ψ_2-plane, ψ_m-ψ_2, rather than the full potential difference across the interface, ψ_m-ψ_s [1] (see Figure 1.3). The phenomenon of loss of the driving force from the applied potential is called iR drop and it is a dynamic process dependent on the flow of current which is causing further imbalance in the charge distribution across the electrode – solution interface.

1.3.   Adsorption at Electrode Surfaces

Adsorption is the binding of species from the solution phase to the electrode surface. The adsorbates may be atoms, ions, molecules, reactant, intermediate, or product of the electrode reaction regardless of whether they are organic or inorganic in their nature. Whatever they are, adsorbates do affect the reaction rate as well as the mechanism involved at the electrode of interest. Adsorption of both organic and inorganic species involving either ions or even neutral molecules can occur at the

electrode surface and in variety of environments. For instance, consider a covalent

bond formed at the electrode surface for the next following reactions, e.g.

$$H^+ + e^- + Pt \leftrightarrow Pt\text{-}H \qquad\qquad (1.6)$$

$$CH_3OH + 2Pt \leftrightarrow Pt\text{-}CH_2H^+ + Pt\text{-}H \qquad\qquad (1.7)$$
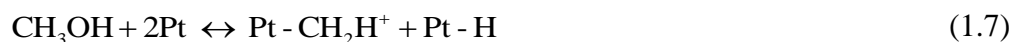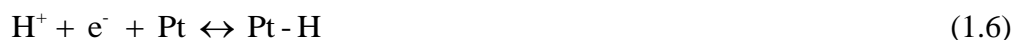
In addition to covalent bonding-based technique, adsorption can also occur by means

of electrostatic forces. This can be achieved if the electrode surface is electrostatically

charged with either positive or negative which eventually attracts ions or dipoles with

opposite charge to it. The accumulation species with counter charge enable adsorption

via electrostatic method to be achieved. An example of a reversible adsorption

process is shown in equation (1.6), meanwhile an irreversible one can be represented

as shown in equation (1.7) [1]. Feasibility to adsorb electroactive species of interest

from solution onto the electrode surface at open circuit is a great plus, but one can

always vary the surface charge simply by varying the electrical potential applied to

the electrode surface. Generating a positively or negatively charged electrode surface

is also a very simple process as it only requires the application of required potential to

the electrode of interest.

1.4. Mass Transport

The supply of reactant and removal of product to / from the electrode surface are

essential to a continuing chemical change. In order electron transfer to occur, the

reactants have to transport themselves towards the electrode surface, and once the

reaction is complete the product will automatically diffuses away from the electrode

surface. Generally, there are three different modes of transportations, diffusion, convection, and migration.

Diffusion. In nature the difference of concentration between two points in a solution normally ends up with a movement of a more concentrated species to the area of the less. This will last until the concentration between them reaches equality. This phenomenon which originates from the concentration gradient is called diffusion [1]. Diffusion plays an important role when considering a reaction an electrode. Very often, the electron transfer process occurs at the vicinity of an electrode. For example, when a species O undergo a reduction process at a considerable rate to become R at the electrode, in theory it shall be considered that the concentration of the former at the electrode surface is lower than at the bulk solution. In other words, the concentration of the reduced species R at the electrode surface will be higher than in the bulk solution. Fick's first law defines diffusion as diffusional flux which represents the number of moles diffusing per unit area (see Eq 1.8). Fick then derived his second law which applies to cases whereas the change of concentration within a specific area is thought (see Eq 1.9) [6]. In these equations, j_{ox} is the flux, D is the diffusion coefficient, [Ox] is the concentration of the species, and x is the distance of the species from the electrode surface.

$$j_{ox} = -D_{ox} \frac{\partial [Ox]}{\partial x} \qquad (1.8)$$

$$\frac{\partial [Ox]}{\partial t} = -D_{ox} \frac{\partial^2 [Ox]}{\partial x^2} \qquad (1.9)$$

In most of the electrochemical measurements where the oxidation and reduction of active species due to the applied electrical potential are concerned, the Fick's second law is more preferable as both former processes always result in changes of concentration at the electrode surface with the elapse of time.

Convection. The presence of thermal gradient or difference in density within a solution can lead to another form of mass transport namely convection. Convection may occur in nature or deliberately induced by means of applying external forces such as shaking or sparging the solution in the electrochemical cell where the electrode reaction is considered. In general, in an unstirred solution, convection is always caused by the chemical reaction at the adjacent of electrode surface which probably generates slight changes in density or even temperature. Meanwhile, unnatural convection is always considered as unfavourable as these changes eventually induce the movement within the cell solution. Very often, in electrochemical experiments, convection can be controlled by flowing the electrolyte solution over the electrode surface at a known rate or by the usage of rotating disc electrode [4].

Migration. Migration by definition is a form of mass transport which originates from the potential gradient induced by the movement of charged species such as ions in the electrochemical cells. As in all electrochemical experiments, the application of electrical voltages between electrodes which generates the passing of current between the former involves the creation of potential drop at the electrode | electrolyte solution surface. Migration, which occurs due to the electrostatic forces is an integral part of the electrode reaction consideration since it balances any changes in charge capacity. However, it is not compulsorily desired in all circumstances of electrochemical

reactions. To overcome this problem, very often the addition or usage of supporting

electrolyte solution to the electroactive solution is a common practice as it helps

minimizing the effect of migration. It shall be noted that although the reactant or

product in the electrode cell may be charged species, with the presence of excess

electrolyte solution, they will be enclosed by the ions of the supporting electrolyte

solution, therefore these ions are the charged species which moves, not the

electroactive themselves [1].
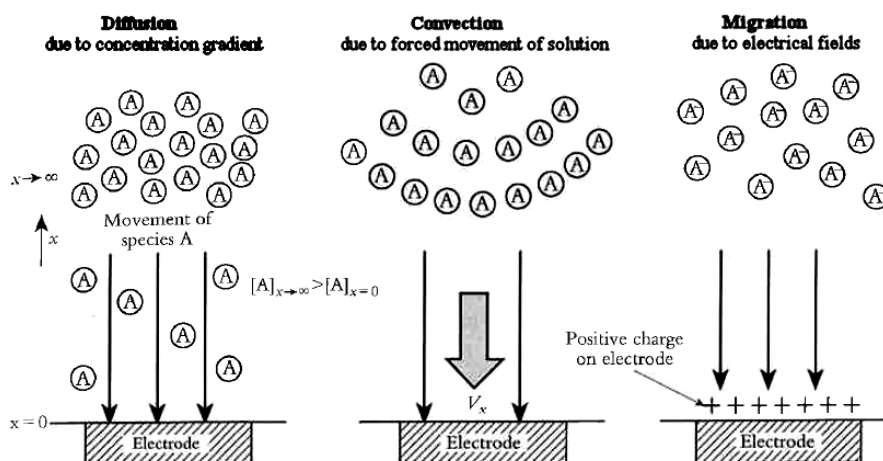
Figure 1.4 Three different forms of mass transport for electroative species in solution
to the electrode surface [4].

1.5. Voltammetric Techniques

1.5.1 Electrochemical Experimental Considerations

Electrochemistry is the study of electron transfer reactions between electrodes and reactant molecules, usually, and as this report is concerned, in the solution phase. In this work particularly, techniques used for the study of these reactions include linear sweep voltammetry, cyclic voltammetry and potential step voltammetry. There are many experimental set ups that can be used to carry out these measurements but the most common used is the three electrode cell. This involves placing the working electrode, reference electrode counter electrode into a cell containing a solution of the redox system under investigation and an inert background electrolyte. The solution is purged of oxygen with nitrogen or argon gas and the experiment is controlled using a potentiostat and personal computer.
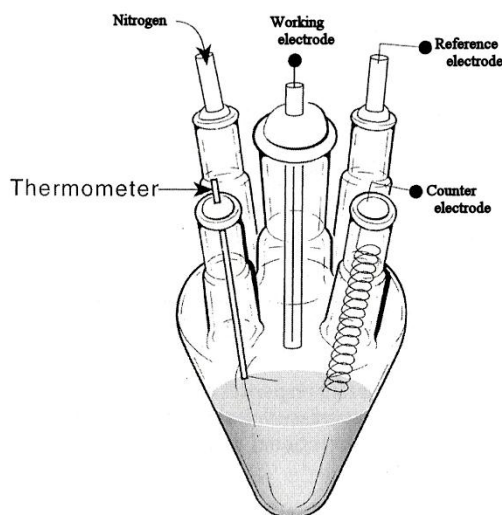
Figure 1.5   Standard electrochemical cell consisting of three electrodes, reference electrode, working electrode, and counter electrode.

The most important part when conducting voltammetric measurements is the apparatus, called potentiostat. It acts as a potential provider to the electrochemical cell and gives out the resulting flowing current. The output of a voltammetric scan is called voltammogram, which shows the relationship between the applied potential and the current produced. Modern potentiostats in general employ a three-electrode setup as shown in Figure 1.5.

Typically, the potential difference is applied between a reference electrode and a working electrode. Since that electron transfer occurs at the working electrode, it is of vital importance so as to ensure that consistent measurements between the former electrode is possible, thus the counter electrode is then introduced into the cell. However, two-electrode experimental system is possible only when the conducting current is low. In this case, counter electrode is not needed and experiments can be performed using only the reference electrode and working electrode.

There are varieties of working electrodes available depending on the experimental purposes. As far as this investigation is concerned, the working electrodes include bare glassy carbon electrode, modified basal plane pyrolitic (bppg) electrodes (with metallophtalocyanine groups and TODAQ), and modified ITO electrodes (with nanoparticles and DNA strands).

The simplest counter electrode (used in this investigation) is normally composed of a piece of platinum wire with a large surface area, and often immersed directly into the cell solution during measurements. The reason for having a reasonable large area relative to the working electrode is not to limit the flowing of current in the total

circuit. Supposed that current resulting from a reduction process takes place at the working electrode, to balance out, an oxidation process then will occur at the counter electrode and vice versa. In large scale experimental setups where measurements are taken over a long timescale, accumulation of products at the counter electrode may happen. To circumvent this problem, salt bridges are sometimes used.

A reference electrode is essential as it provides a stable potential base relative to the working electrode of interest. Some of the mostly used reference electrodes may include the followings:

(a) Standard hydrogen electrode (SHE)

   $Pt \mid H_2(g)$, $H^+(aq)$
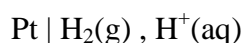
(b) Saturated calomel electrode (SCE) (used in this investigation)

   $Hg \mid Hg_2Cl_2$ (s), KCl (aq)
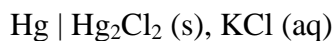
(c) Silver-silver chloride electrode

   $Ag \mid AgCl$ (s), KCl(aq)
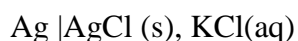
With the potential of 0 V at all temperatures, it may sound very convenient to use SHE electrode in experiments. However, SHE is prone to physical poisoning and cannot be used in solutions which contain redox species, making it unsuitable for repeated usage. Reference electrode consists of a metal in contact with its sparingly soluble salts, immersed in a saturated salt solution that contains common anions such

as saturated calomel electrode (SCE) and silver-silver chloride electrode are more stable for long timescale experiments.

Very often that solutions, which can be defined as a mixture of conducting electrolyte and the electroactive species, are used as solvent in electrochemical experiments. Vase majority of electrochemical setups use water as a solvent, while other options include organic based solvents are also common. The bottom line when selecting a solvent for a particular experiment is to ensure that it does not allow high concentration of electrolyte solution to be formed to obtain a solution with a reasonable conductivity. Another important aspect to consider would be its compatibility with chemistry that occurs at the electrode surface and that the reactants for the electrode process has an acceptable level of solubility required for the reaction of interest.

Addition of supporting electrolytes with high degree of ionization is essential so as to provide sufficient conductivity of the solution. Increasing amount of electrolytes makes the solution less resistive, in other words, facilitates the flowing of current occurring from the interfacial electrode process. It is also vital to keep the electrode-solution distance so that the potential drop shall be maintained in the range of 10-20 Å to allow smooth electron tunnelling as well as to avoid from the migration effect in the solution. Presence of additional supporting electrolytes also helps in keeping the ionic strength constant throughout the electrolysis. This is because of the relatively high concentration of supporting electrolytes to reactants and products. It also contributes in holding the activity coefficients for both reactants and product equal so that they will cancel out in the Nernst equation.

Most fundamental setups in electrochemical cell are designed with an inert gas inlet/outlet. This is required so as to minimize the interference of signals from oxygen molecules during experiments. Nitrogen gas and argon gas are two most well-known examples of inert gas. Nitrogen is always preferred for its low cost, while argon sometimes is another option as it is heavier than air.

1.5.2. Equilibrium Conditions

The simplest electrochemical measurement can be made when equilibrium is reached between a metallic electrode (m) and a redox active species in an aqueous solution phase (aq). For a general one electron transfer process the following equation can be written:

$$O(aq) + e^-(m) \leftrightarrow R(aq) \tag{1.10}$$
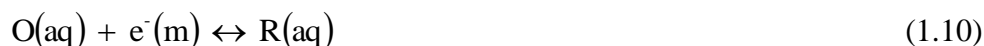
Where the oxidized species O can be reduced at the electrode surface to the species R (or vice versa). As the reaction involves the transfer of an electron between two distinct phases and as the reaction moves towards equilibrium, a net charge separation occurs between the electrode and the solution. This charge separation creates a potential difference at the electrode-solution interface.

The potential difference is fixed for a particular system providing no current is passed through the system. This can be measured simply by placing a reference electrode into the solution and attaching it to the working electrode via a voltmeter. The potential difference is then measured relative to the standard reference electrode, which by

convention has a potential difference of zero. Since no current is drawn through the cell, the equilibrium potential reached is dependent on the relative concentrations of the species O and R. Nernst[1] showed that for a particular system the equilibrium potential, E_{eqm}, could be calculated from equation 1.11.

$$E_{eqm} = E^0 + \frac{RT}{F} \ln \frac{[O]}{[R]} \tag{1.11}$$

Here E^0 is the standard electrode potential, R is the gas constant, T is the absolute temperature, n the number of electrons transferred per molecule, F is the Faraday constant, and [O]/[R] the concentration ratio of the species at the electrode surface, which under equilibrium conditions is the same as the bulk. From equilibrium measurements thermodynamics parameters such as free energies, entropies, enthalpies and equilibrium constants can be calculated for the system.

1.5.3. Nernst Equation

Most of reactions in electrochemistry will involve heterogeneous electron transfer between the working electrode and the redox active species in the solution. Normally the redox active species will have to diffuse towards the electrode surface, and once it is in the electrode surface region, the redox form will be subject to either homogeneous or heterogeneous chemical reactions that may be accompanied by the electron transfer. If the electron transfer rate is extremely fast relative to the mass transfer of the redox active species, then the electrode reaction is said to be reversible.

Under this condition, the ratio concentrations of oxidized and reduced forms of the redox couple can be described by so-called Nernst equation.

In electrochemical measurements, energy is being supplied in the form of electrical voltage. This energy source is the driving force of all possible chemical reactions. In redox reactions, the movement of charged particles (may be electrons or ions) always give rise to potential difference between the electrode and the solution. The maximum potential difference is called the electromotive force (EMF), E, and the maximum electric work W is the product of charge, q, in Coulomb (C), and the potential ΔE in Volt (J/C).

$$W(J) = q\Delta E \qquad\qquad (1.12)$$

Since that the Gibbs free energy, ΔG, takes the opposite sign of the maximum electric work, it can be written as

$$\Delta G = -W = -q\Delta E \qquad\qquad (1.13$$

In a redox reaction, definite amounts of reactants and products are clearly stated. The number of electrons taking place in the reaction is also proportional to the amount of charge transferred in order to complete the reaction. The Faraday constant, F, defines that one mole electron contains a charge of 96485 C. Thus,

$$q = nF \qquad\qquad (1.14)$$

and,

$$\Delta G = -nF\Delta E \qquad (1.15)$$

At standard conditions, the Gibbs free energy can be written as

$$\Delta G^0 = -nF\Delta E^0 \qquad (1.166)$$

The Nernst equation represents the correlation between the Gibb's Free Energy and EMF in a chemical reaction or also known as the galvanic cell. Consider a reaction scheme below

$$aA + bB \leftrightarrow cC + dD \qquad (1.17)$$

As changes in Gibb's Free Energy, ΔG, can be shown as

$$\Delta G = \Delta G^0 + RT\ln Q \qquad (1.18)$$

and

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (1.19)$$

Combining equation 1.16 and equation 1.18 will give

$$\Delta G = -nF\Delta E = \Delta G^0 + RT \ln Q \qquad\qquad (1.19$$

Therefore

$$-nF\Delta E = -nF\Delta E^0 + RT \ln Q \qquad\qquad (1.20)$$

Thus, the above equation can be re-written as

$$\Delta E = \Delta E^o - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad\qquad (1.21$$

In a simple reaction as shown in equation 8, the above Nernst equation can be simplified as

$$\Delta E = \Delta E^o - \frac{RT}{nF} \ln \frac{[R]}{[O]} \qquad\qquad (1.22$$

or

$$\Delta E = \Delta E^o + \frac{RT}{nF} \ln \frac{[O]}{[R]} \qquad\qquad (1.23$$

At equilibrium, $\Delta E = 0$, to result in

$$0 = \Delta E^o - \frac{RT}{nF} \ln \frac{[R]}{[O]} \qquad\qquad (1.24$$

Thus,

$$E_{eqm} = \Delta E^o = \frac{RT}{nF} \ln \frac{[R]}{[O]}$$ (1.25

It shall be emphasized that when the electron transfer rate is too small relative to the

mass transfer rate, the observed current will not be a function of the mass transport. In

such case, the Nernst equation is no longer applicable.

1.5.4. Electrolysis

Electrochemical cells can be operated under conditions where a current flows and this

is achieved by applying a potential that is different to E_{qm}. The current induces the

exchange of electrons between the electrode and molecule in solution. This can

happen in either direction so that O is reduced to R:

$$O(aq) + e^-(m) \rightarrow R(aq)$$ (1.27)

or so that R can be oxidized to O:

$$R(aq) \leftrightarrow O(aq) + e^-(m)$$ (1.28)

The magnitude of the current is given by equation 1.29.

$$I = AFj \qquad\qquad\qquad\qquad (1.26$$

Here A is the area electrode, F is the Faraday constant and j is the flux of electroactive species reaching the electrode surface. The flux, j, in turn is related to the concentration of the reactant at the electrode surface, $[O]^0$, and also the heterogeneous rate constant, k^0, for the electrochemical reaction (see equation 1.30).

$$j = k^0 [O]^0 \qquad\qquad\qquad\qquad (1.30)$$

The heterogeneous rate for the transfer of an electron may depend on several steps of the reaction. This includes the concentration of the reactant species O at the electrode surface, which is different from that in the bulk and depends on the method of mass transport taking place in the cell. These typically are diffusion, convection and migration and need to be taken into account in an experiment or eliminated as much as possible by stirring or by using the rotating disc electrode. The electron transfer step is a quantum-mechanical tunnelling process. Similarly to chemical reactions the transition state model can be used to describe the electron transfer, where there action path involves the reactants overcoming an energy becoming product.
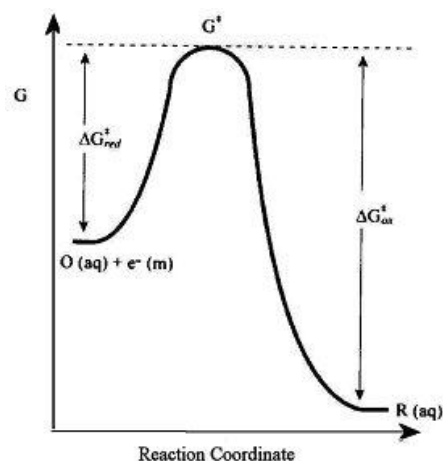
Figure 1.6 Free energy plot for a one-electron reduction of O(aq).

In Figure 1.6 electron transfer is possible when the transition state is reached and the rate determining step is linked to the vibrational reorganisation of the system including redox active molecule and solvent shell [7]. The heterogeneous standard rate constant for electron transfer, k_{red}, is predicted as shown in equation 1.31.

$$k_{red} = A\exp\left(\frac{-\Delta G^{*}_{red}}{RT}\right)$$

(1.27

ΔG^{*}_{red} is the free energy of activation and A is a frequency factor to account for the number of collisions of the molecules with the electrode. Importantly the rate constant for both cases can, in turn, be controlled but the electrical potential applied to the system and more accurately the over potential are required for the reaction to take place.

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1.5.5. Overpotential and Energy Levels

A pure crystal contains a lattice of closely packed atoms whose atomic orbitals will all be of a similar energy and so overlap. Instead of considering them as discrete energy levels, the orbitals can be thought of as bands; the valence band which is analogous to the HOMO and the conductance band which can be thought of as the LUMO. In a metal there is no gap between the valence and conductance and so the bands overlap and electrons can move freely through the metal. The level of the band up to which electrons occupy is called the Fermi level and an electrical potential applied to a metal acts to increase or decrease the energy of the Fermi level.

For an electron transfer to occur between the electrode and species O, the Fermi level must be higher than LUMO of the species O. In the figure below, the Fermi level is below the LUMO and so the process is unfavourable and reduction does not occur. However, if the Fermi level in the metal is raised by the application of a negative electrical potential to above the LUMO of O, the electron transfer becomes favourable. The electrical potential that must be applied to a system, above E_{eqm}, in order to make the electron transfer process favourable is called the overpotential, η.
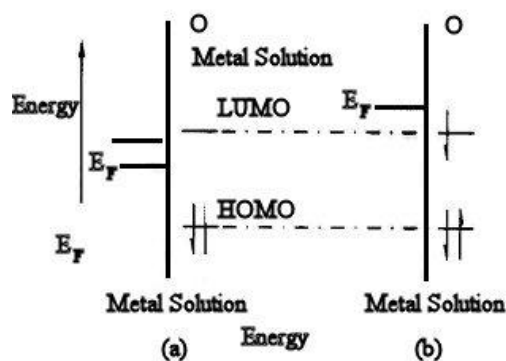
Figure 1.7 Representation of electronic energy levels when (a) the Fermi level is too low for electron transfer to occur and (b) at a level where the electron transfer process becomes favourable.

1.5.6. Cyclic Voltammetry

Linear sweep voltammetry works simply by changing the potential of the working electrode from a set value of E_2 to E_1 usually from a situation where electron transfer does not occur to one where it is driven rapidly. As the change in potential is set over a specific time, then it is a measurement of the change in current over both a potential and time range.
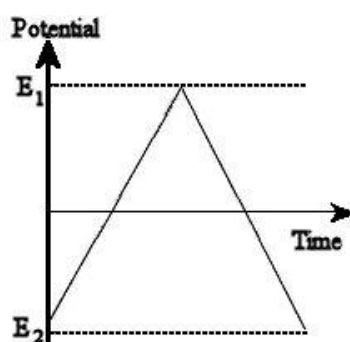
Figure 1.8 Variation of potential with time during a cyclic voltammetry experiment.

Meanwhile, cyclic voltammetry (CV) is an extension of linear sweep voltammetry so that once E_2 is reached, the direction of the sweep is reversed and the electrode potential is scanned back to E_1. CV has become an important and widely used electroanalytical technique in many areas of chemistry. It is rarely used for quantitative determinations, but it is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products. This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed. The response obtained from a CV can be very simple, as shown in Figure 1.9 for the reversible redox system:
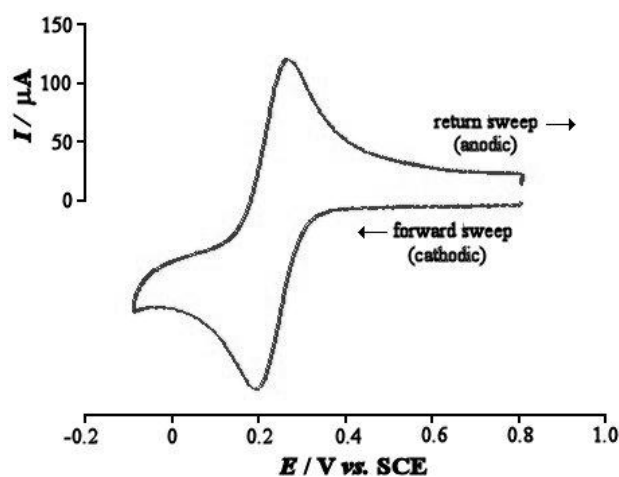
Figure 1.9 Simple reversible cyclic voltammogram.

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A stationary working electrode, usually a platinum disc, in an unstirred solution is employed, and the potential is varied at a finite rate as a linear function of time. Typical sweep rates are in the range of 0.5 - 100 V s^{-1}, and the current potential curves no longer have the S-shape known from techniques with infinitesimally small sweep rates, but exhibit peaks. If a rapid triangular sweep is applied, and an oscilloscope or a fast x-y recorder is used a cyclic voltammogram is obtained. If, for example, the sweep towards lower potentials produces reduced molecules in the vicinity of the electrode, then they are re-oxidized during the reverse sweep to the same concentration which was initially present in the solution, provided that the rate at which the potential is taken back to its initial value is more rapid than the diffusion processes needed to establish equilibrium with the bulk of the solution. If the reduced species undergoes irreversible secondary reactions in a shorter period than that of triangular sweep, then new waves may be found in the reverse sweep and the height of the wave corresponding to the forward reaction is reduced.

The peak current i_p in this voltammogram is given by Randles-Sevcik equation (1.28).

$$i_p = \left(2.69 \times 10^5\right) n^{3/2} A D^{1/2} \upsilon^{1/2} C \qquad\qquad (1.28)$$

Here i_p is the peak current (in amperes), n is the number of electrons passed per molecule of analyte oxidized or reduced, A is the electrode area (in cm^2), D is the diffusion coefficient of analyte (in cm^2 s^{-1}), v is the potential sweep rate (in V s^{-1}), and C is the concentration of analyte in bulk solution (in mol cm^{-3}).

The midpoint potential of the two peaks in the voltammogram is given by

$$E_{mid} = \frac{E_{red} + E_{ox}}{2} \qquad\qquad (1.28$$

The midpoint potential E_{mid} can written as shown in equation 1.33. Here, E_{red} is the reduction potential, E_{ox} is the oxidation potential, and n is the number of electrons transferred per molecule.

The maximum potential E_p in the current-potential curve in the linear scan voltammetric experiment for a reversible one-electron transfer is given by equation 1.34.

$$E_p = E_{1/2} - \frac{28.5}{n} \qquad mV \text{ at } 25°C \qquad\qquad (1.29$$

Finally, the separation between the two peaks of the voltammogram is given by

$$\Delta E_p = E_{ox} - E_{red} = 2.4RTnF = 59 \, mV/n \quad (at \, 25^oC) \qquad\qquad (1.30$$

Hence, depending on what is already known about a given system, one could determine the concentration, the diffusion coefficient, the number of electrons per molecule of analyte oxidized or reduced, and/or the redox potential for the analyte, all from a single experiment.

On the reverse scan, the position of the reoxidation peak is not identical with the potential of the forward scan. It depends on the switching potential, if the reverse

sweep starts at less than 100 mV/n cathodic of the reduction peak. If the switching potential however, is set further apart, the separation of the two peaks will be 57 mV/n and is independent of the scan rate of the potential scan. These two criterion, together with the equal height of the steps in the forward and reverse reactions, are commonly taken as diagnostic for reversible, purely diffusion controlled charge transfer, and cyclic voltammetry has been used simply to obtain potentials which could also have been measured by slow techniques, and at the same time to demonstrate reversibility of the electron transfers.

If the scan rate in cyclic voltammetry is increased to values greater than 0.1 V s^{-1}, then the redox couples do not behave like ideal reversible systems because electron transfer rates are not infinitely large and the current is controlled by a mixture of diffusion and charge transfer kinetics. This is called the *quasi-reversible* case and cyclic at varying scan rates can be used to measure electron transfer rates. Detailed discussion on the reversibility in electrochemical measurement will be presented in the later section.

1.5.7. Reversible and Irreversible Reactions

The term reversible is always misunderstood and sometimes can be confusing in chemistry as it has two different meanings depending on the context of the reaction. In general reversibility can be divided into two categories; chemical and electrochemical.

In order to explain the term 'reversible' clearly, the following simple reaction shall be considered.

$$O + ne^{-} \leftrightarrow R \tag{1.36}$$

The reaction scheme shows that the reactant, in the reduced form, is being transformed into a product by means of having an n number of electron on the time scale of the voltammetric experiment. From the chemical point of view, this Ox/Red couple can be reproduced chemically as represented by the double-sided arrow. Therefore the oxidation reaction can then be expressed as

$$R \leftrightarrow O + ne^{-} \tag{1.37}$$

Meanwhile, the heterogeneous process taking place between a metal working electrode and an electroactive species at the vicinity of the electrode surface results in electron transfer. In electrochemical experiments, electron transfer can be affected by the potential applied and the concentration of the electroctive species at the electrode. Therefore the rate constants play very important role in determining the electrochemical reversibility of a reaction.

Using the same chemically reversible reaction scheme above, electrochemical reversibility can be explained the following way. Supposed that the rate constants for reduction and oxidation as k_{red} and k_{ox} respectively.

$$O + ne^{-} \rightarrow R \tag{1.38}$$

When the applied potential is equal to E^{0} of the redox couple at equilibrium, the standard electrochemical rate constant can be represented as k^{o} and will have the units,

cm s^{-1}, derived from the concentration of electroactive species shown in mol cm^{-3} and electron transfer to the electrode surface with surface area in cm^2. Here rate constant for electron transfer in both forward and backward direction of the above reaction scheme can be represented in the following manner

$$k_{red} = k^0 \exp\left(\frac{-\alpha_{red} nFE}{RT}\right)$$
(1.31

$$k_{ox} = k_{red} \exp\left(\frac{\alpha_{ox} nFE}{RT}\right)$$
(1.40)

Here the rate constants for both reduction and oxidation processes driven by the potential difference or overpotential, $\eta = E - E_0$, from the applied electrical potential, E, can be shown by

$$k_{red} = k^0 \exp\left(\frac{-\alpha_{red} nF(E - E_0)}{RT}\right)$$
(1.41)

$$k_{ox} = k^0 \exp\left(\frac{-\alpha_{OX} nF(E - E_0)}{RT}\right)$$
(1.42)

k^o is the rate constant at the electrode surface at equilibrium, α_{red} is the cathodic transfer coefficient, α_{ox} is the anodic transfer coefficient, and R is the gas constant (8.314 (V C) / (mol K)). α is defined as the fraction of the interfacial potential at an electrode-solution interface that helps in lowering the activation energy barrier for electron transfer process.

Another way to derive the equation of standard electrochemical rate constant is by comparing the equation representing the diffusion layer, $\delta_{diffusion}$, with that of the reaction layer, $\delta_{reaction}$. The reaction layer, $\delta_{reaction}$, is best described as the diffusion layer at a particular scan rate of interest .

$$\delta_{diffusion} = \sqrt{\frac{D}{\upsilon}} \qquad (1.43)$$

$$\delta_{reaction} = \frac{D}{k^0} \qquad (1.44)$$

It shall be noted that at the transition point, from reversible to irreversible condition, the thickness of the diffusion layer and the reaction layer is equal. Therefore,

$$\frac{D}{k^0} = \sqrt{\frac{D}{\upsilon}} \qquad (1.32$$

If a constant RT/F is multiplied to both sides of the equations,

$$\frac{D}{k^0} = \sqrt{\frac{DRT}{\upsilon F}} \qquad (1.33$$

To give

$$k^0 = \sqrt{\frac{D\upsilon F}{RT}} \qquad (1.34$$

It shall be noted that under room temperature the diffusion coefficient shall take the value of $D = 10^{-9}$ m^2 s^{-1}. Based on the equation 1.47, by substituting various values of potential scan rates, the corresponding k^0 can be determined accordingly. The following table can be used in dictating the electrochemical reversibility.

$k^o > 0.020$ cm s^{-1}	reversible
5.0×10^{-5} cm s$^{-1} < k^o <$ 0.020 cm s^{-1}	quasi-reversible
$k^o < 5.0 \times 10^{-5}$ cm s^{-1}	irreversible

Table 1 Dictation of electrochemical reversibility of a reaction.

Although electrochemically reversibility of reaction can be determined from the above figures, it is also very useful to use a more practical approach when cyclic voltammetric experiments are conducted in the laboratory. This method has proven to be extremely helpful when voltammetric responses are being measured within a wide range of scan rates as it is a common practice to record voltammograms over a wide potential window so as to determine the reversibility of a reaction. In practice, there are three parameters which can be used.

(a)Peak to peak separation, ΔE_{pp}.

In a reversible voltammogram, the magnitude of the peak to peak separation, $\Delta E_{pp,}$ shall be approximately 57 mV at room temperature (298 K) regardless of scan rate values. On the contrary, in the case of quasi- and irreversible conditions, the ΔE_{pp} will depend on the potential sweep rate.

b) Peak current, I_p.

In both reversible and irreversible conditions, the peak current generated is always proportional to the square root of the scan rate values. However, as for quasi-reversible, scan rate does not hold any effects. At room temperature (at 298 K) a simple one electron reduction of O to R can be simplified by

Reversible

$$I_p = 0.446 FA[O]_{bulk} \sqrt{\frac{FD\upsilon}{RT}}$$

(1.35

$$= 2.69 \times 10^5 AD^{1/2}[O]_{bulk} \sqrt{\upsilon}$$

(1.36

Irreversible

$$I_p = 0.49 \sqrt{\alpha} FA[O]_{bulk} \sqrt{\frac{FD\upsilon}{RT}}$$

(1.50)

$$= 2.99 \times 10^5 \alpha D^{1/2}[O]_{bulk} A \sqrt{\upsilon}$$

(1.51)

It shall be noted that under room temperature as for the parameters involved, these following assumptions shall apply; electrode surface area, $A = 1$ cm^2, concentration of species O, $[O] = 10^{-3}$ M, charge transfer coefficient, $\alpha = \beta = 0.5$ cm s^{-1}, diffusion coefficient for species O and R, $D_0 = D_R = 10^{-5}$ cm^2 s^{-1}.

c) Waveshape of the forward peak.

The difference between the peak current potential, E_p, and half peak current potential, $E_{1/2}$, can come in handy when distinguishing a reversible voltammetric signal from an irreversible one as shown below. All the values for the parameters used in the equations correspond to those of at room temperature (at 298 K).

Under reversible condition,

$$\left|E_p - E_{1/2}\right| = \left|2.218\frac{RT}{F}\right| \tag{1.52}$$

whereas under irreversible reduction

$$\left|E_p - E_{1/2}\right| = \left|1.857\frac{RT}{F}\right| \tag{1.53}$$

or

$$\left|E_p - E_{1/2}\right| = \frac{44.7}{\alpha}mV \tag{1.54}$$

and under irreversible oxidation

$$\left|E_p - E_{1/2}\right| = 1.857\frac{RT}{(1-\alpha)F} \tag{1.37}$$

1.5.8. Differential Pulse Voltammetry

The characteristics of the linear sweep and cyclic voltammetric methods hitherto discussed in the previous section has revealed that they are very useful analytical tools in electrochemical measurements as the maximum current flowing resulting from the electroactive species in the solution is proportional to its concentration, thus a very sensitive electroanalytical method. A close relationship between current and concentration gives quantitative information on the system studied and this can be clearly seen if diffusion controls the current magnitude. Although sensitivity-wise, they are undeniably a superior method, it lacks the ability to distinguish between faradaic and capacitive currents thus there is a need for complimentary method to complete the relevant information of interest.

Meanwhile, in differential pulse voltammetry, DPV, fixed voltage pulses are superimposed on a linear potential ramp and are applied to the working electrode at a period of selected time just before the potential pulse drops. The current will be measured twice, which first at a point just before the pulse is being imposed, and then again just before the pulse begins to drop. The interesting point in DPV is that when a potential pulse is applied to an electrode, the capacitive current flows proportionally to it, but decays exponentially with time. The magnitude of the faradaic current, on the other hand, decreases as an exponential function versus $(t)^{1/2}$.

Figure 1.10 shows a typical diagram on how potential pulses, approximately for 50 milli-seconds, are applied on a linear ramp. The first current measured, $i(t_1)$ will be subtracted from the second one, $i(t_2)$, and the difference [$\Delta t = i(t_2) - i(t_1)$] will be plotted against the applied potential. The resulting voltammogram will show current

peaks which are in direct proportion with the concentration of the electroactive species of interest.
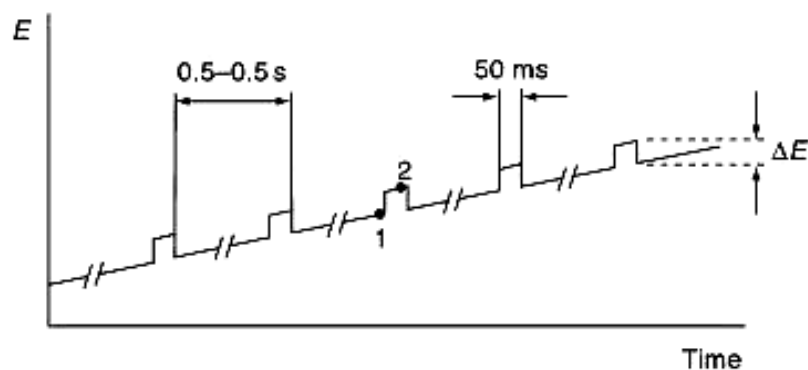
Figure 1.10   Excitation signal for differential–pulse voltammetry.

In DPV, the charging current contribution is so small, about more than an order of magnitude than that of normal-pulse voltammetry, that it is negligible. Conversely, the Faradaic current decays accordingly to the square root of time, producing an excellent signal to noise ratio. Due to these significantly enhanced characteristics, DPV enables the detection at a nano-molar level (1 µg L^{-1}) thus proving hugely useful in electrochemical sensing applications.

1.5.9. Ion Transfer at Triple Phase Boundary (TPB)

A phase boundary is created whenever two or more immiscible phases are brought to contact with each other. As a simple case, if a hydrophobic phase is brought close to a hydrophilic phase, a phase boundary represented as liquid | liquid is said to be formed. In a more advanced situation, when a solid phase electrode is placed into a liquid | liquid system made up of an organic phase and an aqueous phase, a triple phase boundary is created. Figure 1.11A explains the situation in where a conventional

liquid | liquid interface is created, while Figure 1.11B illustrates the formation of a

TPB.
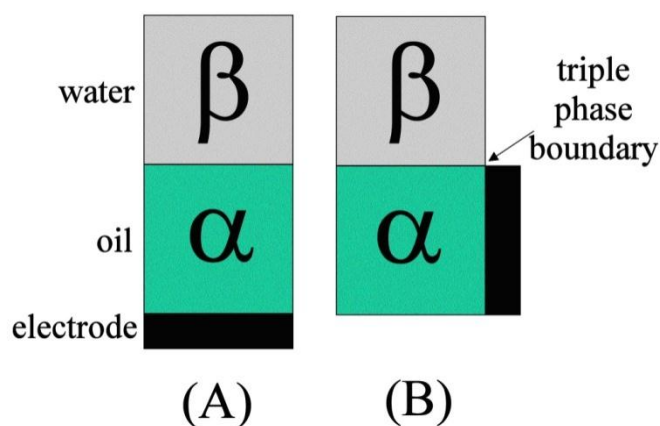
Figure 1.11 Schematic showing (A) a conventional liquid | liquid interface and (B) a liquid | liquid | solid interface, forming a triple phase boundary [8].

A study of the electrode processes occur at the TPB was studied by Marken et al. where a microdroplets of a very higly water insoluble N,N,N,N-tetrahexylphenylenediamine (THPD) is deposited onto a solid electrode and then completed immersed in a aqueous solution consists of totally supporting electrolyte. In this study, the electrode potential was first scanned in a selected potential window (0 to 0.6 V), followed by a visual inspection of the electrode by a microscope. It was observed that a formation coloured ring-like area was confirmed at the TPB. Further investigation by chemical microanalysis disclosed the fact that during the oxidation of THPD, the anions have to move across the liquid | liquid phase boundary and forcedly transported into the organic phase microdroplets (see Figure 1.12b). When the potential scanning was then performed in a negative range, expulsion of anions was then observed [9]. This proves that the insertion / expulsion of anions at the TPB is a reversible process (see Figure 1.12c). Following that, changing the types of anions

and pH in the aqueous phase helps to understand the tell-tale shift in the oxidation potential [10]. The potential shift due to the different types of anions is mainly caused by the Gibbs energy of ion transfer (required energy for anion to cross liquid | liquid phase boundary), while the effect of different pH values explains the applicability of Nernst equation when a transition from an anion exchange to proton exchange is considered [**Error! Bookmark not defined.**].
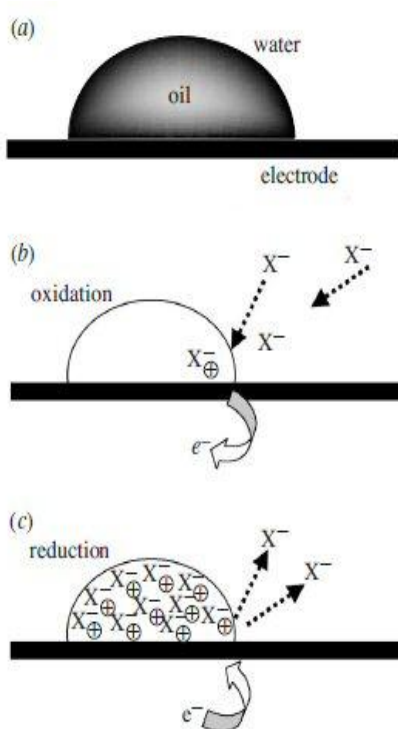
Figure 1.12 Schematic of (a) an oil droplet forming a three-phase junction with an aqueous phase and the electrode; (b) an oxidation process within the droplet, triggering anion transfer from the aqueous into the oil phase; (c) the reverse reduction process, triggering the expulsion of anions into the aqueous phase.

The oxidation of the microdroplets causes the organic phase to possess positive charge, and to balance this out, anions needs to move into the organic from the aqueous solution. This redox process can only happen at the vicinity of the TPB

(liquid | liquid and solid | liquid interfaces). Ball *et al.* proposed that convection partly contributes in maintaining an effective charge transfer at these interfaces [11].

The study of electrochemically driven ion transfer at the TPB has developed a lot in recent years and proven to be a very useful tool especially in elucidating the biological and physiological processes. A compilation of Gibbs free energies measured at the TPB for anions such as amino acids [12], oligo-peptides [13], anionic drugs [14], and cations [15] revealed voltammetric is a reliable method in providing these information.

A combination of having organic microdroplets and a TPB makes it feasible for the study of ion exchange processes to be carried out without the usage of electrolyte to provide for electrical conductivity as electron transfer can take place at the electrode | organic | aqueous electrolyte interface. In Chapter 3 and Chapter 4, the concept of TPB and formation of organic phase microdroplets is exploited.

In Chapter 3, this technique is used to study electrochemical processes for a novel system, microdroplets of 4-(3-phenylpropyl)pyridine (PPP) containing an electroactive MPc is immobilized at basal pyrolytic graphite (bppg) electrode. The organic solvent PPP is non-volatile, highly water immiscible, and a suitable medium for water insoluble transition metal complexes such as those of phthalocyanines. Altogether, a simple quantitative CO_2 detection will be shown. Meanwhile, in Chapter 4, using the same concept, a redox active material, namely TODAQ is incorporated into microdroplets of NOP deposited onto glassy carbon electrode, and pH sensing application will be discussed.

1.6. Surface Characterization Techniques

1.6.1. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was first commercially invented in the 1960's. It is an imaging technique used to determine topological structure particularly that of sample surfaces. SEM gained its popularity due to its ability to produce images with resolution in the 10 nm range, about 1000 times better than that of any other optical microscope. Figure 1.13 shows a schematic of a typical SEM.

The basic operating scheme of an SEM can be illustrated as shown in Figure 1.13. At the electron gun, high energy electron beam of typically 10 keV are generated. The electron gun is normally made of a tungsten filament of where a massive magnitude of current is flown through it. The filament is heated up to around 2700 K so that the thermionic emission temperature is reached. In a Field Emission Gun (FEGSEM), instead of tungsten filament, a sharply-pointed single crystal tungsten wire fabricated by means of electrolytic etching method is used. Through the tunnelling effect, the electrons are sent out from the FEG. This is achieved as the sharp tip contains a high electric field around it enabling it to extract electrons out of the cathode. These electrons then are passaged below the potential barrier. Unlike the tungsten, the FEG cathode is at room temperature and requires clean vacuum environment .

Using a series of scan coils, a minute beam is produced from the emitted electrons which then will be forwarded to the sample. The direction of the beam can be changed variably as required towards the sample by controlling the current flowing through the

scan coils which is held more positive relative to the electron gun so as to separate them from the filament.

There are a few most likely effects that may follow whenever electrons are directed to the sample surface. Electrons may hit the sample surface and rebound without energy loss, or they may be absorbed by the sample to generate emission of secondary electrons, whose energy is lower called secondary electron, together with X-rays. Other probable consequence is that the electrons may be absorbed by the sample, but this it will produce emission of visible light, which effect is known as cathodoluminiscence or cause the sample to be electrified to produce current within it. Any of these effects can be used to generate information on the sample, but it is very commonplace that the secondary electrons take the role to generate sample images.
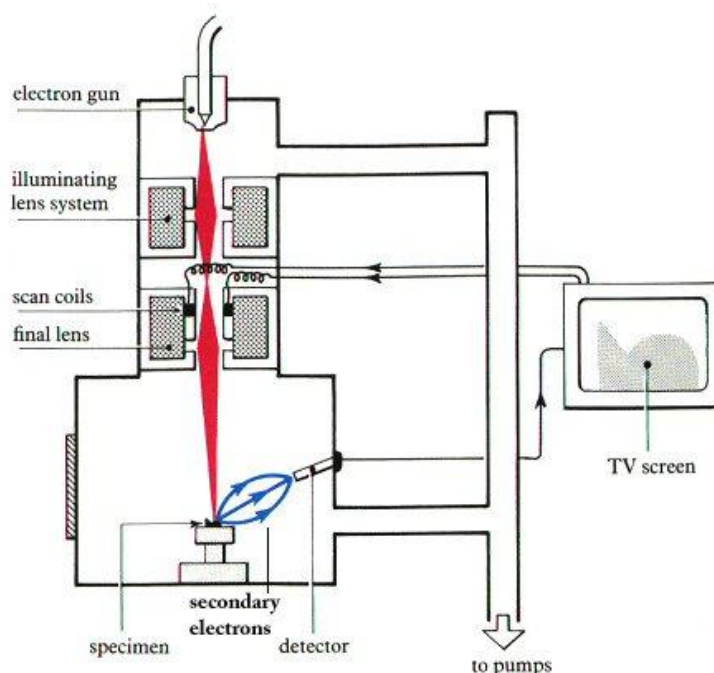

Figure 1.13 Schematic drawing of an SEM [16].

Selection of secondary electrons is performed by drawing them to a grid at a low positive potential approximately 50 V relative to the sample. At the rear side of the grid, a disc coated with a scintillator, (a material that absorb energy and re-release it in the form of light) normally aluminium, so that each time the electrons reach them emission of light would be seen. A photomultiplier tube then detects the light emitted and convert this into a voltage signal. The magnitude of the resulting voltage is proportional to the amount of electrons colliding with the disc. The voltage produced is then focused out to an electronic console which processes and amplifies this signal to create point of brightness on a cathode ray tube or a tv screen.

The images produced by the sample on the tv screen is built up by scanning the electron beam over it simultaneously with the scan of the electron beam in the cathode ray tube. In contrast to optical microscopes, the SEM is not able to magnify the resulting image through contact lenses. Alternatively, a close up look on the sample is gained by altering the ratio of the area scanned to the area of the TV screen. Often, to increase magnification of the SEM images, a smaller restricted area of the sample is first selected and then the electron beam is scanned across it. Occasionally, artefacts resulted from the charging effect are observed in the sample image but can be minimized by evaporating a thin conductive layer on the sample.

1.6.2. Energy Dispersive X-ray Spectroscopy (EDX)

The ability to view three dimensional images of samples of interest does not always solve a problem in an analysis. Occasionally, further complimentary techniques are required to for example when there is a necessity to identify the different elements co-exist within the same sample. For such cases, a typically built-in spectrometer called

Energy Dispersive X-ray Spectrometer (EDS) will be extremely helpful. This non-invasive method is sometimes referred as EDS or EDAX analysis, and used in conjunction with SEM but does not stand alone without the latter.

To further explain, an electron beam hits a sample surface which will be pre-coated to make it conducting. The energy supplied by the electron beam is normally in the region of 10-20 keV. This energy supplies sufficient force for some electrons from the atoms on the sample surface to be knocked off. The vacation of electron from the atom inner shell then filled by the transfer of electrons from the atom outer shell. As the energy levels of the outer shell electrons are higher than that of the inner, the energy difference is then emitted as x-ray.

During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray. Since that the every atom dissipates unique energy level for each electron transfer, identification of the atom from which the x-ray was emitted can be established.

The results from the EDX analysis is called EDX spectrum. In principle it shows a plot of frequency of x-ray emission has occurred for each energy level. As each peak is unique for each atoms, quantitative or qualitative analysis of elemental

composition can be resolved. Higher peaks value simply means a higher concentration of the element is.

Not only that EDX is responsive towards the element according to each peak, it can also reveals the type of X-ray to which it corresponds as well. Each emission from one electron orbital to another carries difference values of energy level and can be represented as in Figure 1.14.
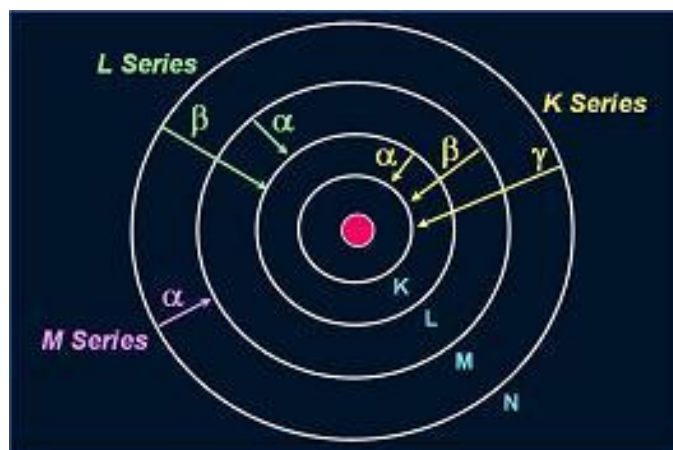
Figure 1.14   Elements in an EDS spectrum are identified based on the energy content of the X-rays emitted by their electrons as these electrons transfer from a higher-energy shell to a lower-energy one [17].

1.6.3. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) belongs to the family of Scanning probe microscopes (SPM), used to study topology of a wide variety of samples. AFM is particularly used in surfaces imaging and in measurement of surface morphology. In principle, AFM operates based on the interaction between the tip and the sample surface. In an AFM a fixed force is kept between the tip and the sample while the probe being rastered across the sample surface, with a tip-probe separation less than

0.5nm. Compared to other conventional optical microscopes, for instance, Scanning Electron Microscopy (SEM), which offers imaging resolution in the order of a few nm, AFM allows a better resolution in atomic scales taken in a three dimensions. Unlike the previous which requires complicated measurement settings such the necessity of having an electrically conductive samples or sample pre-treatments to avoid charge build-up, and the needs for samples to be vacuum compatible so as to allow electron tunnelling to create images, the latter does not need the samples to be conductive nor vacuum environment, and imaging can be performed both in solid and liquid states even at low temperatures These simple features of AFM allows significant development to expand in many fields especially of materials science, chemistry, biology, and physics. A typical set-up of an AFM is depicted in Figure 1.11(A).
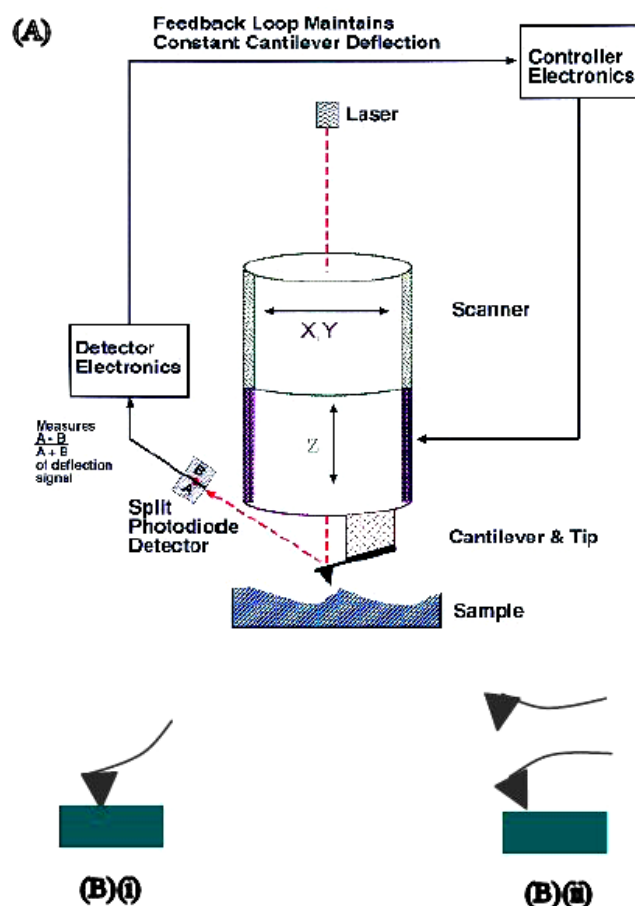
(A) Feedback Loop Maintains Constant Cantilever Deflection

Controller Electronics

Laser

Scanner

X, Y

Detector Electronics

Measures A - B / A + B of deflection signal

Z

Split Photodiode Detector

Cantilever & Tip

Sample

(B)(i) **(B)(ii)**

Figure 1.15 Schematic diagram of an AFM. The sample is placed on the piezoelectric scanner. A laser is reflected off the upper side of the cantilever and into a split photodiode via a mirror. In this way, vertical (z) and horizontal (y) deflection signals can be measured [18].

Contact mode and non-contact mode are two among few available scanning probes modes in AFM which have become commonplace in surface imaging. The working mechanism of the contact mode AFM is shown in Figure 115(B)(i).

Contact mode AFM is one of the most widely used method in scanning probes which works based on rastering a sharp tip across the sample. The force works on the tip is repulsive. Initially, the AFM tip needs to be moved manually very close to the vicinity of the sample. The piezoelectric scanner then will automatically adjust the position between the cantilever tip and the sample based on the pre-setup distance value

decided beforehand. Now that the sample is in direct contact with the sample surface, it will then be scanned by a piezoelectric scanner by means of either moving the sample or tip relative to each other. Every deflection resulted from the scanning causes the laser beam at the back of the cantilever tip to be reflected off to a split photodiode. This photodiode acts as a sensor which records all the deflections produced from the scanning. In order to maintain a constant distance between the cantilever tip and the sample, a feed loop is used in where the scanning direction is adjusted in the z direction. By having a feedback loop, damages caused to the sample from crashing of the cantilever tip could be minimized although cannot be totally eliminated. The measured cantilever deflections are used to generate a map of the surface topography. This technique has proven to be an effective method for imaging of biological samples. Although contact mode AFM offers fast scanning rate and proven to be very useful when having samples with rough surface area, often the force imposed end up causing damages or deformation of soft samples and distortion of the image as a consequence. This problem is always encountered with softer materials, such as biological samples, polymers, and even some seemingly hard materials, such as silicon wafers. This problem is however resolved by imaging in liquid form.

To overcome the problem that may arise from contact mode AFM, a so-called intermittent mode or tapping mode has been developed. The imaging principle is very similar to that of the previous but differs in terms of the way the cantilever tip oscillates. In tapping mode AFM, the tip is deflected at a certain intervals or resonant frequency, Figure 1.15B(ii). This way, the cantilever tip lightly taps the sample surface during rastering process and only touches the sample surface on a single oscillation. This method has proven to be a powerful tool when dealing with samples

that are prone to be damaged or loosely held to a surface. However, the difficulty to perform imaging in liquid form limits its advantages [19].

1.7.   Innovation in Electrochemical Sensing

Electrochemical sensors have nowadays become an integral part in our everyday lives. Starting from the simplest disposable glucose sensor to the most complicated machines ever exist, they all differ in their designs and fabrication methods depending on the intended usage or purposes. Theoretically, an electrochemical sensor consists of two main elements, a receptor and a transducer. A receptor is normally the part having a direct contact with the sample. Very often, a receptor consists of a thin layer of film deposited on an inert substrate or electrode. The transducer, on the other hand, is a major element in any electrochemical sensor as it plays a major role in processing and converting any changes or parameters in the system into discernible signals, frequently in the form of current, voltage, or impedance/conductance. The recent rapid development in sensing field imposes a lot of impact on the construction of these sensors. In this section, a brief discussion on the general characteristics, elements and common methods indispensable in the construction of fundamental electrochemical sensing devices, with the emphasis on the sensor receptor will be discussed.

Currently, starting from the laboratory method to the industrial, there are varieties of options available for the fabrication of films. Thick films in general are defined as layers possessing a thickness of less than 0.1 μM. Thick-film technology normally is a major part inmicroelectronics, and normally refers to the screen printing technology in

where selected materials in paste form (sometimes called ink) are immobilized on a substrate with sieves to form a desired structure. The inks used to spread film pattern normally contains leads which may contain gold, platinum, palladium and glassy carbon particles. Usually, ceramic materials are chosen for thin films fabricated at high temperature. The film patterns are normally formed using CVD method. Meanwhile, thin-film fabrication normally utilizes the semiconducting and mechanical properties of highly purified crystalline silicon as the base. The manufacturing steps of thin-film may include covering by metallic layers, followed by the making of etching masks using photolithography, etching processes and covering of insulating layers. There are several deposition methods of materials onto substrates, for example via high vacuum deposition, sputter deposition or by chemical procedures such as CVD. A good example of thin film is the inter-digitated electrode of where the structure resembles an overlapping two combs.

In order for the receptor to interact with the target compound, the substrate or electrode surface will normally have to undergo two key processes, surface cleaning and surface modification. In this work, all the working electrodes (bppg carbon, GC and ITO) go through cleaning step either by polishing with micro-sized abrasives, followed by sonication. These treatments are essentials in electrochemical sensing in order to remove any impurities or adsorbed layers prior to usage. Subsequently, the pre-treated substrates will then undergo a modification procedure to provide the receptor base with functional groups or molecules for particular applications.

Ideally, the modified surface shall have a certain level of stability in order to be used repeatedly and durable for a certain length of time for sensing purposes.

Immobilization of chemical and biological compounds for surface modification has long been a useful method be it for quantitative or qualitative measurements. There are many methods available for surface modification such as adsorption, and covalent attachment at the surface. In this work, modification of working electrode surface was achieved *via* evaporation method and layer by layer deposition method, which will be discussed in detailed in the corresponding chapters. The usage of metallo-intercalators for binding of biological molecules such DNAs will also be presented in this work.

Regardless of types of electrochemical sensors, there are common facts that apply to them. First of all, sensors, in a broader sense shall interact with the target / sample directly at the surface. It shall also be emphasized that electrochemical sensors shall be able to convert or transform the chemical signals into electrical signals at a reasonable time length. Preferably, they shall exhibit certain level of repeatability to be able to work continuously.

In this work, focus of attention is first put on the usage of functional materials such as cobalt(II)phthalocyanine owing to its well known redox properties in the literature. The electrochemical properties of the said material is characterized in relation to the triple phase boundary graphite | 4-(-3-phenylpropyl) pyridine | aqueous electrolyte processses which leads to its application in CO_2 sensing. The next highlight is then directed to the new organic redox system observed in TODAQ. Previous studies of Anthraquinone derivaties have demonstrated their capability of exhibiting sensitivity towards proton as well as cation exchange properties. The immobilization of TODAQ in organic liquids coupled to the triple phase boundary process promotes the construction of a basic pH and cations sensing system. Then, a new type of thin film

is constructed from alternating functionalized positively charged carbon nanoparticles and negatively charged DNA target probe *via* layer by layer deposition method. The detection of dsDNA via this method will be shown. Following that, an elegant way of constructing an ammonia sensor by means of having an ionomer-matrix experimental setup using functional CNPs and ion exchangers for pH sensitive application will be discussed. Finally, fundamental properties of Prussian blue-decorated ion exchanger matrix system are studied, and feasible applications will be proposed.

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to 12 pH range and Dowex 50 1x2 has been demonstrated to allow control of the local pH at the electrode. Although most experiments were performed with 80% relative humidity under argon, it has been shown that sensitivity of the device towards humidity changes is acceptable. Injection of ammonia into the argon gas flow has been employed to cause pH changes at the electrode surface as monitored by the L-dopa-boc oxidation differential pulse peak potential. Sensitivity levels of 1 cm^3 ammonia (or ca. 33000 ppm short term exposure) are readily achieved in particular at lower L-dopa-boc-modified carbon nanoparticle loadings. In future, this device concept will be of wider use and potentially important for cases where chemical selectivity in gas sensing is required. For example, specific surface immobilised receptor groups could be developed to allow disease bio-marker detection in breath or environmental pollutant detection in urban or office areas.

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