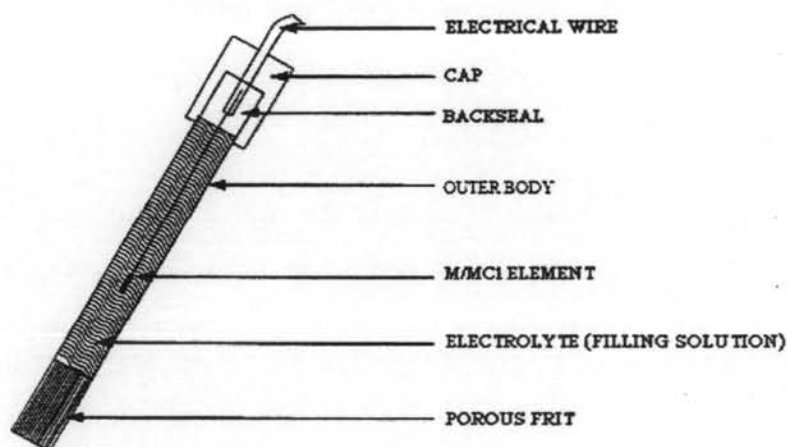


## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Reference Electrode

Reference electrodes are designed so that there is a well defined potential difference between the metal electrode and the solution in contact with it. The term reference electrode refers to a system which includes an electrode and the solution in which the electrode is immersed. All these components are enclosed in a chamber with a junction connecting the internal filling solution with the solution in the cell. The reference potential depends on the composition of the fill solution and the metal-metal salt or metal oxide that constitutes the electrode element. The fill solution must be protected from dilution and/or contamination through the junction. Ordinary reference electrodes have the components shown below in Figure 2.1



**Figure 2.1** Components of a typical reference electrode.

Theoretically, any reaction can be used as a reference, as long as it can be maintained in equilibrium at the electrode surface. An ideal reference should be independent of time and should be reproducible regardless of the variation of temperature (Komarek, 1992). It has been shown that a correction algorithm of

electrode potential can be independent of the solution composition for a wide range of neutral and alkaline solutions (Bosch *et al.*, 2003)

## 2.2 Nernst Equation

In order to calculate the electrode potential, the Nernst equation is usually applied. The Nernst equation generally correlates with the Gibbs free energy ( $\Delta G$ ) and EMF of the electrochemical cell. For the reaction;



where  $\nu$  are stoichiometric coefficients.

The Nernst equation is related to the Gibbs free energy, as is shown in the following derivation;

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_R^{\nu_R}}{a_O^{\nu_O}} \quad (2)$$

and

$$\Delta G = -nFE \quad (3)$$

Therefore,

$$-nFE = -nFE^\circ + RT \ln \frac{a_R^{\nu_R}}{a_O^{\nu_O}} \quad (4)$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_R^{\nu_R}}{a_O^{\nu_O}} = E^\circ - \frac{RT}{nF} \ln \frac{\gamma_R^{\nu_R} [R]^{\nu_R}}{\gamma_O^{\nu_O} [O]^{\nu_O}} \quad (5)$$

$$E = E^* - \frac{RT}{nF} \ln \frac{[R]^{\nu_R}}{[O]^{\nu_O}}; E^* = E^\circ - \frac{RT}{nF} \ln \frac{\gamma_R^{\nu_R}}{\gamma_O^{\nu_O}} \quad (6)$$

Where  $R =$  Gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T =$  Temperature (K)

$n =$  Number of electron transferred in the reaction

$F =$  Faraday constant ( $96485 \text{ C/mol}$ )

$\gamma_i =$  activity coefficient of species  $i$

$a_i =$  activity of species  $i$

### 2.3 Activity ( $a$ )

The Activity of a component is used to account for the non-ideality of a system. For ideal solutions, cations and anions do not interact with each other whereas in a real solution, ions with opposite charges are more likely to attract one another. Therefore the chemical potential on one ion will be affected by others in the solution. The difference in the chemical potential of an ion in a real solution as compared with the ideal solution is due to the electrostatic force between ions. The positive ion electrostatically attracts anions and repels cations. The activity is defined as;

$$a_i = \gamma_i C_i \quad (7)$$

Where  $\gamma_i$  is activity coefficient of species  $i$

$C_i$  is ionic molarity ( $\text{mol L}^{-1}$ )

Since the activity coefficient can not be directly calculated, the Debye Hückel (DH) theory is applied. The DH concept considers a particular ion as a point charge which is immersed in a dielectric solution (water in this case) that has an equal amount of opposite charges around it in a "charge cloud". It has been shown that the non-ideal behavior of an ionic solution is proportional to the Debye Hückel length. This Debye Hückel length describes the distance from the point charge where the potential is maximized. Since the DH theory describes a highly dilute electrolyte

solution, the activity coefficient was found to be proportional to the square root of ionic strength ( $I$ ) where  $I$  is defined as;

$$I = \frac{1}{2} \sum z_i^2 m_i \quad (8)$$

Where  $z_i$  = ionic charge of species  $i$

$m_i$  = molarity of species  $i$

Therefore, the activity coefficient is given by;

$$\ln \gamma_{\pm} = \frac{-A(z_+ z_-) \sqrt{I}}{1 + B \sqrt{I}} \quad (9)$$

Where  $A$  and  $B$  are constants given as 0.5 and 1.5 respectively at room temperature.

Equation (5) can be used to calculate the cell potential of any galvanic cell for any concentration of ions in solution. The reference electrode to which all tabulated values have been measured against is the Standard Hydrogen Electrode (SHE). It is arbitrarily set to zero as shown in Table 2.1.

**Table 2.1** Typical standard cell potentials at 25°C versus SHE

Cathode Half Reaction	$E^0$ (Volts)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Zn}_2^+ + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.7621
$\text{Fe}_2^+ + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.4089
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{SHE})$	0.0000
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.2221
Saturated Calomel (SCE)	+0.2412
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^- + 2\text{Hg}$	+0.2680
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.7991
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.2288
$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.07

From the Nernst equation, there are several parameters which alter the system potential from the standard state; concentration, activity coefficient and temperature. The variation of concentration in the filling solution will affect the measured potential. In order to achieve a stable potential, equilibrium concentrations have to be established. This is normally done by using a concentrated filling solution to keep the equilibrium condition. For example, the filling solution used in a silver/silver chloride electrode is typically saturated potassium chloride. This avoids metal dissolution from the coated metal to the filling solution, which may be passed on to the test solution.

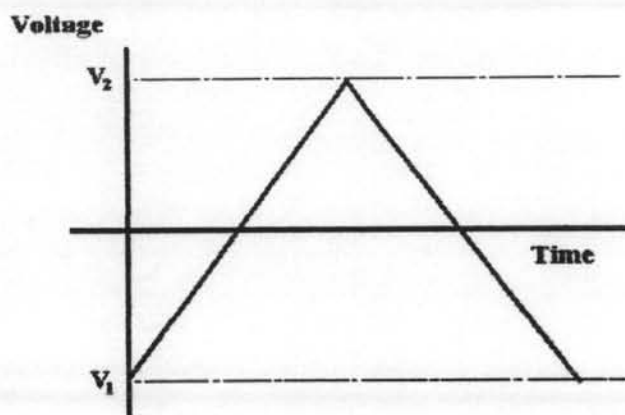
Another parameter that needs to be considered is temperature. In order to calculate the potential as a function of temperature, the activity coefficient as a function of temperature must be known.

Sengarsai, T. (2005) studied the effect of temperature on reference electrodes at high temperatures and high pressures in a titanium autoclave. The potential was found to be inversely proportional to temperature. As the temperature increases, the potential dropped considerably.

However, the Nernst equation can only be applied when the chemical reaction is known. Electrochemical mechanisms can be proposed by using several methods, a common method is cyclic voltammetry.

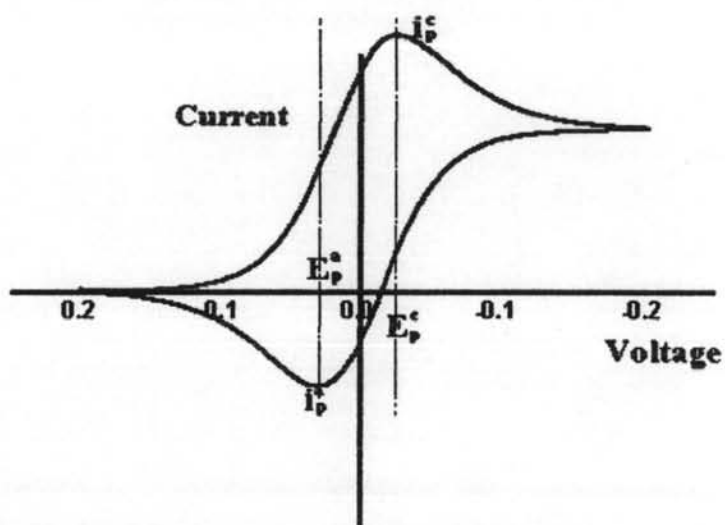
## 2.4 Cyclic Voltammetry (CV)

Cyclic voltammetry is often referred to as electrochemical spectroscopy. It is a commonly used method to study the electrode surface interactions with certain solvents under an electric current. In addition, CV can also be used to determine the reversibility of a redox reaction in the system. Generally, the potential is applied back and forth with respect to time as shown in Figure 2.2.



**Figure 2.2** Potential is applied in both negative and positive direction alternately.

With this measurement, the cathodic and anodic current is obtained at a particular potential. A plot of the current passed against an applied potential will typically resemble the curve in Figure 2.3.



**Figure 2.3** Current characteristic change as the potential is swept.

If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be reversible. The following parameter values are used to characterize the cyclic voltammogram for a reversible process:

1. The peak potential separation,  $\Delta E = E_p^c - E_p^a = \frac{58}{n} mV$  at all scan rates at 25°C.
2. The peak current ratio,  $\frac{i_p^a}{i_p^c} = 1$  at all scan rates.
3. The peak current,  $i_p = 2.69 \times 10^5 n^{3/2} ACD^{1/2} \nu^{1/2}$
4. The peak current function  $\frac{i_p}{\sqrt{\nu}}$  where  $\nu$  is scan rate.

Where  $n$  = number of electrons transferred in the reaction

$A$  = electrode surface area ( $\text{cm}^2$ )

$C$  = concentration ( $\text{mol cm}^{-3}$ )

$D$  = diffusivity of reacting compound ( $\text{cm}^2 \text{s}^{-1}$ )

The cyclic voltammogram was used to investigate the redox reaction of the synthesized lithium ferrite ( $\beta\text{-LiFe}_5\text{O}_8$ ). Two sets of redox peaks were obtained, corresponding to anodic and cathodic peaks (Xiong Wang *et al.*, 2005).

The cyclic voltammetry method has also been used in other areas such as fuel cell applications. Lithium ferrite compounds were alternatively chosen for the cathode material in a molten carbonate fuel cell. Cyclic voltammetry was applied and indicated the peaks which represented the formation of FeO of the surface of Fe. It was also shown that at higher positive potentials, a rapid increase in current is seen. This rapid increase in current was due to the oxidation of FeO to  $\text{LiFeO}_2$ , formation of  $\text{LiFe}_5\text{O}_8$  and chromium oxidation. This enhanced the life time of the cathode in the system (Colonmer *et al.*, 2002).

## 2.5 Mass Transfer

Mass transfer is the movement of material from one location to another, arising from differences in electrical or chemical potential between two locations and solution agitation. Since mass transfer plays an important role in electrochemical dynamics, three different modes of mass transfer are introduced.

2.5.1 Migration The movement of a charged body influenced by an electric field (a gradient of electrical field).

2.5.2 Diffusion The movement of a species influenced by a gradient of chemical potential (concentration gradient for instance).

2.5.3 Convection This includes stirring or hydrodynamic transport. In electrochemical systems, two types of convection can be found, natural convection and forced convection.

Mass transfer to an electrode is governed by the Nernst-Planck equation. One dimensional mass transfer along the x-axis can be written as

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi_i(x)}{\partial x} + C_i v(x) \quad (10)$$

Where

$J_i(x)$  = the flux of species i at distance x from the surface ( $\text{mol s}^{-1} \text{cm}^{-2}$ ).

$D_i$  = the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )

$\frac{\partial C_i(x)}{\partial x}$  = the concentration gradient at distance x ( $\text{mol cm}^{-2}$ )

$\frac{\partial \phi_i(x)}{\partial x}$  = the potential gradient ( $\text{V cm}^{-1}$ )

$z_i$  = charge

$C_i$  = concentration of species i ( $\text{mol cm}^{-3}$ )

$v(x)$  = velocity in which elements move along the axis ( $\text{cm s}^{-1}$ ).

A general electrochemical system is frequently designed so that one or more of the contributions to mass transfer are negligible. For example, the migrational component can be reduced by addition of an inert electrolyte at a concentration much larger than that of the electroactive species. Convection can be avoided by preventing stirring and vibrations in the electrochemical system. Neglecting these, a reduced form of the Nernst-Planck equation is obtained as;



$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} \quad (11)$$

This is also known as Fick's First Law.

To combine mass transfer with the Nernst equation, several parameters need to be introduced. Since the net rate of electrode reaction,  $\nu_{rn}$ , is governed by the rate at which the species is brought to the surface by mass transfer,  $\nu_{mt}$ ;

$$\nu_{rn} = \nu_{mt} = \frac{i}{nFA} \quad (12)$$

Where  $i/A$  = current density ( $A\text{ cm}^{-2}$ )

Since the unit of current is the charge per unit time, it is also designated as the electrode reaction rate, the rate at which the charges are transferred from one location to another.

From the Fick's First Law, the rate of mass transfer is proportional to the concentration gradient at the electrode surface

$$\nu_{mt} \propto \left( \frac{dC_o}{dx} \right)_{x=0} = D_o \left( \frac{dC_o}{dx} \right)_{x=0} \quad (13)$$

If the concentration gradient is assumed to be linear within the diffusion layer, then

$$\begin{aligned} \nu_{mt} &= D_o [C_o^* - C_o(x=0)] / \delta_o \\ \nu_{mt} &= m_o [C_o^* - C_o(x=0)] \end{aligned} \quad (14)$$

Where  $\delta_o$  is introduced to combine with the diffusion coefficient to produce  $m_o$ , which is the mass transfer coefficient ( $\text{cm s}^{-1}$ ). This constant can also be seen as volume flow rate per unit area ( $\text{cm}^3 \text{s}^{-1} \text{cm}^{-2}$ ). The (\*) term designates the species concentration in bulk solution. Substituting (12) into (14), yields

$$\frac{i}{nFA} = m_o [C_o^* - C_o(x=0)] \quad (15)$$

Under conditions of net cathodic reaction, R is produced at the electrode surface so that  $C_R(x=0) > C_R^*$  (where  $C_R^*$  is the bulk concentration of R) therefore,

$$\frac{i}{nFA} = m_R [C_R(x=0) - C_R^*] \quad (16)$$

The value of  $C_o(x=0)$  and  $C_R(x=0)$  are functions of electrode potential, E. The largest rate of mass transfer of O occurs when  $C_o(x=0) \ll C_o^*$ , so that  $C_o^* - C_o(x=0) \approx C_o^*$ . the value of the current under these conditions is called the limiting current,  $i_l$  where

$$i_l = nFAm_oC_o^* \quad (17)$$

The presence of a limiting current indicates the maximum rate of mass transfer of species O because it is being reduced as fast as it can be brought to the electrode surface. The expression for  $C_o(x=0)$  can be obtained from equation (15) and (17)

$$C_o(x=0) = \frac{i_l - i}{nFAm_o} \quad (18)$$

If the kinetics of electron transfer are fast, the concentration of O and R at the electrode surface can be assumed to be at equilibrium with the electrode potential, as governed by the Nernst equation for the half-reaction,

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{C_R(x=0)}{C_o(x=0)} \quad (19)$$

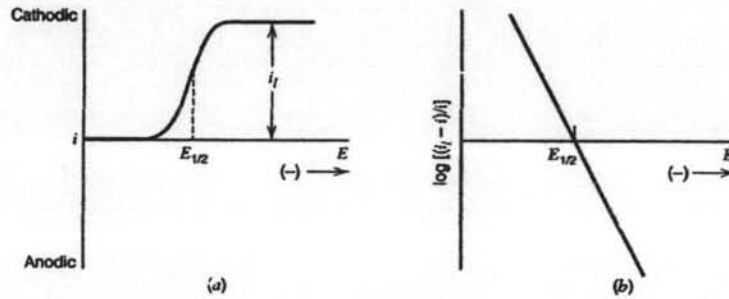
Initially, species R is absent, therefore  $C_R^* = 0$ , therefore

$$C_R(x=0) = \frac{i}{nFAm_R} \quad (20)$$

Combining equations (18) and (20), The Nernst equation can be written as

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{m_R}{m_O} + \ln \frac{i_l - i}{i} \quad (21)$$

From the  $i$ - $E$  plot shown below, Figure 2.4(a) shows that  $I = i_l/2$  when  $E = E_{1/2}$ .



**Figure 2.4 (a)** Current-potential curve for Nernstian reaction with only oxidant present initially. **(b)**  $\log((i_l - i)/i)$  vs  $E$  for this system.

Hence

$$E = E_{1/2} = E^{0'} + \frac{RT}{nF} \ln \frac{m_R}{m_O} \quad (22)$$

$E_{1/2}$  is used to characterize the O/R system and, it is independent of the substrate concentration. Figure 2.4(b) shows the relationship between  $E$  vs  $\log((i_l - i)/i)$ , hence

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_l - i}{i} \quad (23)$$

A plot of  $E$  vs  $\log \frac{i_l - i}{i}$  is a straight line with the slope of  $2.3RT/nF$  (or  $59.1/n$  mV at  $25^\circ\text{C}$ ).

## 2.6 Lithium Ferrite Preparation

Much research and development has been focusing on the synthesis of lithium ferrite compounds. Because of its low cost and environmentally friendly properties, lithium-iron oxide has attracted many researchers' attention.

Xiong Wang *et al.*, (2005) have synthesized ultra fine lithium ferrite ( $\beta$ - $\text{LiFe}_5\text{O}_8$ ) nanoparticles at a low operating temperature ( $140^\circ\text{C}$ ) and their magnetic and electrochemical properties were examined. It was concluded that this type of lithium ferrite compound exhibits higher discharge capacity than other lithium ferrites, as it is used as an active cathode material. It was found to have a unique microstructure achieved by the hydrothermal synthesis procedure.

Another powdered lithium ferrite was prepared by Yen-Pei Fu (2005) by microwave-induced combustion using lithium nitrate, iron nitrate, chromium nitrate and carbonhydraside as starting materials. The powder obtained was annealed at  $650^\circ\text{C}$  for 2 hours and was treated by several methods. This production method has some advantages over solid state reaction preparation such as more homogeneity, finer particle size and less impurities contained in the system.

A spinel-type, well-crystallized, ordered  $\text{LiFe}_5\text{O}_8$  powder was prepared by a sol-gel process (Sung Yong An *et al.*, 2005). Lithium acetate and iron nitrate nonahydrate were used as starting materials and mixed with a ratio of Li/Fe of 1/5. Lithium ferrite powers were treated by an annealing process at different temperatures.

Tabushi *et al.*, (1995) prepared lithium ferrite  $\alpha$ - $\text{LiFe}_5\text{O}_8$  by a hydrothermal method at low temperature ( $130$ - $220^\circ\text{C}$ ) with a large excess amount of lithium hydroxide and ferric nitrate with a Li:Fe ratio of 10:1, followed by a post annealing at  $700^\circ\text{C}$ .

El-Shobaky and Ibrahim (1987) synthesized lithium ferrite by mixing ferric oxide and lithium carbonate in a molar ratio of 1:2 and in an equimolar ratio. This lithium ferrite was studied using DTA, TG DTG and X-ray diffraction techniques. The results show that lithium ferrite ( $\text{LiFe}_5\text{O}_8$ ) was successfully obtained from an equimolar ratio regardless of the spinel type.

Lithium ferrite can be synthesized by many procedures, however, there is no apparent way to obtain lithium ferrite deposits onto a medium and use it for an electrochemical measurement apparatus. If lithium ferrite compounds can be deposited and used as a reference electrode, a beginning of a new technique of electrochemical measurement will be available.