CHAPTER 2

LITERATURE REVIEW

Hydrogen production from fossil fuels contributes to about 90% of the total hydrogen produced in the world (Buddhi et al 2006; Tinoco et al 2008). It can also be produced from thermo-chemical processing of primary energy sources such as coal, natural gas and oil; from renewable energy sources such as methanol or biomass and by electrolysis of water. Out of these methods, water electrolysis process is robust, environmentally benign and has high efficiency (Millet et al 2009; Schulze et al 2002) as water is a clean and cost effective source of hydrogen. Splitting of water to produce hydrogen and oxygen for commercial usage dated back to the 1890. It takes place by passing direct current through water molecules to break into hydrogen and oxygen ions. Water electrolysis integrated with photovoltaics, nuclear power stations or wind turbines is one of the most promising methods for large-scale renewable hydrogen production (Dell & Rand 2008). There are three major ways to produce hydrogen from water; they are electrolysis, photo electrolysis and thermolysis.

2.1 ELECTROLYSIS

Water electrolysis is a process that takes place by passing electricity through water to break apart the water molecule into positive hydrogen (H\(^+\)) and negative oxygen (O\(^-\)) ions (Genders & Weinberg 1992). Among the various methods, water electrolysis is a promising candidate as it simply relies on electricity to split the water molecules into hydrogen and
oxygen ions with minimum voltage ($\Delta V > 1.23V$) for hydrogen production (Murayama & Yamanaka 2011). These hydrogen and oxygen ions migrate towards their respective opposite electrodes leading to formation of diatomic $H_2$ and $O_2$ molecules due to electron transfer (Badwal et al. 2006). However, the process is not efficient enough to be considered as a source for high demand of hydrogen production as the process is rather slow and costly due to high overpotential for the reactions (Pletcher & Walsh 1993). In order to decrease the overpotential catalysts with improved efficiency and processes with reduced resistances (use of solid polymer electrolyte based cells) have been developed (Dell & Rand 2004; Dubey et al 2010). The schematic view of electrolysis of water is shown in Figure 2.1

![Figure 2.1 The schematic view of water electrolysis](image)

Figure 2.1 The schematic view of water electrolysis
Water electrolysis processes may be carried out in the presence of alkaline electrolytes or in the presence of solid polymer membrane based electrolyte. The alkaline electrolysis using potassium hydroxide (KOH) electrolyte and water electrolysis using perfluorinated sulphonic acid membrane as electrolytes are well known and electrolyzer units based on these are commercially available. Each of these two processes has their own advantages and disadvantages with respect to ease of operation, cost and scalability (Herring 2005). The oxygen evolution reaction (OER) is known to possess high activation overpotential in alkaline solutions (Fujiwara et al 2000) resulting in substantial energy losses. The cell reaction is written as follows:

\[ \text{Anode: } H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \quad (2.1) \]
\[ \text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \quad (2.2) \]
\[ \text{Cell reaction: } H_2O \rightarrow \frac{1}{2}O_2 + H_2 \quad (2.3) \]

Liquid water is introduced at the anode and dissociated into molecular oxygen, protons, and electrons. Solvated protons formed at the anode migrate through the membrane to the cathode where they are reduced to molecular hydrogen. During migration of protons through the membrane, water molecules accompany the protons through the membrane from the anode to cathode due to an electric field (Abbas & Daud, 2010). Thus, the
electrolyzer prototype of GHW (Gesellschaft Hochleistungselektrolyseure Wasserstofferzeugung), a German company, delivers hydrogen under 30bar pressure, using the bipolar cell stack assembly with diaphragm unit installed in a framed cells that is completely encapsulated in a pressure vessel. The main operating cost of this process is the cost of electrical power which is used to activate the charge transfer reactions at the electrode-electrolyte interface and to overcome the resistivity of the electrolyte (Wuebbles & Jain 2001). A lowering of the electrolytic energy consumption is required in order to make AWE technology more efficient.

The electrolysis of aqueous alkaline solutions has historically been one of the most popular routes for hydrogen production (Rasten et al 2003; Kamnev et al 1992). The AWE is characterised by the use of a strongly alkaline aqueous solution of 25-30 wt. % KOH to maximise the ionic conductivity, as the hydroxide ions (OH) are the charge carriers (Lu & Srinivasan 1978). The reactions that take place in the electrolysis cells of these units are:

Anode: \( 2OH^- \rightarrow \frac{1}{2}O_2 + 2e^- + H_2O \) (2.4)

Cathode: \( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \) (2.5)

Cell reaction: \( H_2O \rightarrow \frac{1}{2}O_2 + H_2 \) (2.6)

The OER Equation (2.4) is known to have high activation...
that take place and affect the hydrogen production. First is activation loss that occurs at low currents, next is the ohmic loss that takes place throughout the process and final type of loss is the concentration loss that occurs at high currents (Sherif et al 2005). As the applied voltage is increased, the electrode surface absorbs the gas till it reaches a certain saturation point where the gas pressure at the electrodes equals the level of external air pressure and gas bubbles begin to rise at the electrodes. Thus the current density determines the rate of bubble growth and influences bubble coalescence on the electrode surface (Smolinka 2009). The movement of the electrolyte in the form of convection and electrolyte flow rate influences the mass transport in the electrolyte. In general, electrochemical reactions are governed by mass transfer limitations at higher operating current densities (Wendt & Kreysa 1999).

Materials with high catalytic activity and low over potential are required for the OER. Nickel based alloys are low cost and their wide availability together with low overpotential for the OER makes them the material of choice as anodes in alkaline water electrolysis (Brossard & Marquis 1993; Oesten & Huggins 1995; Casella & Contursi 2012). Dixit et al (1996) have reported significant reductions in oxygen over potential with electrodeposited nickel alloys with transition metals. In general an alkaline water electrolyzer operates with a low current density (< 0.4A/cm²) with platinum free electrodes that can easily be manufactured. Therefore, suitable catalyst materials and methods to improve performance of water electrolysis techniques are always under development (Zeng & Zhang 2010; Millet et al 2011). The purpose of electro catalyst is to reduce the cell voltage either by increasing the catalytic surface area of the electrode or by changing the catalytic nature of the over potential of the reaction. In AWE anodic overpotential is a major factor in limiting efficiency and is hence the most frequently studied reaction (Haverkamp et al 2011; Carmo et al 2013).
Although, RuO$_2$ and IrO$_2$ (Hoseinieh & Ashrafizadeh 2013, Mayousse et al 2011, Pauli & Trasatti 2002, Panic et al 2006) exhibit lowest overpotential for OER, their poor long term stability and cost prohibits their use in commercial cells. Ni based electrodes due to their excellent corrosion stability in alkaline solution (Tasić et al 2013) is an alternative low cost solution despite its higher overpotential when compared to RuO$_2$ and IrO$_2$ (Lee et al 2011; Goodenough et al 1989). Hall (1985) has studied nickel anodes in alkaline water electrolysis and concluded that nickel could be used more efficiently, primarily by increasing its electrochemically-active surface areas, particularly those based on mixed metal oxides showed great promise. The incorporation of zinc in nickel based electrodes increases surface area, catalytic activity and lowers over voltage. It has also been found that the presence of sulphur increases the rate of detachment of gas bubbles from the electrode surface and decreases the over voltage, thus increasing the current density (Lupi et al 2011).

AWE thus offers many advantages as it is a well-established process that uses non noble metal based catalysts which are cost effective and with which multi cell-stacks may be built for commercial applications (Bockris & Otagawa 1984; Singh et al 2007). The disadvantages of the system include the use of corrosive electrolyte, operation at low current densities.

2.3 THERMODYNAMICS

From a thermodynamic point of view, the electrolysis of water reaction is a non-spontaneous reaction. The driving force is providing energy externally to the system, for example, electricity. Thus the term ‘electrolysis’ comes from a combination of two Greek words: ‘elektron’ meaning current and ‘lysis’ meaning to separate. Therefore, in a water electrolysis system, electricity is used to split water molecules into gaseous hydrogen and oxygen.
The principle reaction of electrolysis can be expressed by:

$$\text{H}_2\text{O (liq)} \rightarrow \frac{3}{2}\text{O}_2 (g) + \text{H}_2(g) \quad (2.7)$$

The equation of energy change is:

$$\Delta H = \Delta G + T\Delta S \quad (2.8)$$

In the above equation, T is absolute temperature; $\Delta H$ is the change in enthalpy; $\Delta S$ is entropy change; and $\Delta G$ is the Gibb’s Free Energy. At equilibrium, the amount of electricity ($nFE$) required to split 1mol of water is equal to the change in $\Delta G$ of the water dissociation reaction (Momirlan & Veziroglu 1999).

$$\Delta G = -nFE = -2FE \quad (2.9)$$

where ‘$n$’ is the number of electrons exchanged during the electrochemical splitting of water ($n=2$): *F is the Faraday’s constant* (96,500 C/mol) and $E$ is the thermodynamic voltage (V)

The minimum electrical energy demand for electrolysis of water decreases with increasing temperature (Douglas et al 2013). The decrease of electrical energy demand leads to higher electrical efficiency (Marangio et al 2011). High operating temperature also generally improves electrode kinetics rate. $\Delta G$ is a function of both operating temperature and pressure and thus Equation (2.9) becomes:

$$\Delta G(T, P) = \Delta H(T, P) - T\Delta S(T, P) > 0 \quad (2.10)$$

To split 1mole of water molecules, $\Delta G$ (J/mol) of electricity and $T\Delta S$ (J/mol) of heat are also required. The thermodynamic electrolysis potential $E$ in volt and voltage $V$ are defined as:
\( E (T, P) = \frac{\Delta G (T, P)}{nF} \) \hspace{1cm} (2.11)

\( V (T, P) = \frac{\Delta H (T, P)}{nF} \) \hspace{1cm} (2.12)

Under standard conditions of temperature (298 K) and pressure (P= 1 atm), \( \text{H}_2\text{O} \) in liquid state, with \( \text{H}_2 \) and \( \text{O}_2 \) in gaseous state, the standard free energy, entropy, and enthalpy changes for reaction (Equation 2.10 & 2.11) are

\[ \Delta G^o (\text{H}_2\text{O}) = E^o = \frac{\Delta \epsilon^o (\text{H}_2\text{O})}{2F} = 1.23 \text{ V} \] \hspace{1cm} (2.13)

Hence the cell voltage of 1.23V is required and an additional voltage term \( T\Delta S^o/2F \) should also be added to the thermodynamic voltage \( E \) to provide the heat required by reaction. The minimum amount of energy that needs to be applied as electrical energy (Bard & Faulkner 2001) is given by

\[ \Delta H_R = \Delta G_R + Q \] \hspace{1cm} (2.14)

where \( \Delta H_R \) is the enthalpy of reaction of water splitting; \( \Delta G_R \) is the Gibbs free energy of reaction and the term ‘Q’ is the amount of energy that needs to be applied as heat. The reversible voltage \( V_R \) is related to the electric energy demand, \( \Delta G_R \), of the cell in ‘n’ amount of electrons exchanged in the electrochemical reaction

\[ V_R = \Delta G_R / nF \] \hspace{1cm} (2.15)

Thus the overall efficiency of the system can increase because of improved kinetics and reduced ohmic drop with increase in temperature (Degiorgis et al 2007). Thus the equation becomes

\[ \varepsilon = \frac{\Delta H}{\Delta G + \text{losses}} \] \hspace{1cm} (2.16)
The differences of theoretical and experimental efficiencies are due to three main types of losses that take place and affect the hydrogen production. Activation loss that occurs at low currents, ohmic loss that takes place throughout the process, and concentration loss that is significant at high currents. This can be explained by the schematic view of polarisation curve shown in Figure 2.2.

![Figure 2.2 Polarisation curve for water electrolysis](image)

**Figure 2.2 Polarisation curve for water electrolysis**

A typical polarization curve showing the current density-voltage relation for water electrolysis is shown in Figure 2.2. There is an initial drop in the cell potential due to activation polarization, followed by a long linear rise in voltage due to ohmic losses, and then a sharp knee in the potential due to the concentration polarisation (Onda et al. 2004). Thus the components of the cell voltage is represented as

\[ E = E' + \eta_{(s, a)} + \eta_{(s, c)} + IR + \eta_{(C, a)} + \eta_{(C, c)} \]  

(2.17)
where, $\eta$ is the overpotential, ‘a’ and ‘c’ are anode and cathode compartments; ‘s’ and ‘C’ are surface and concentrations terms in overpotential. Where ‘I’ is the current flowing through the resistance ‘R’ and ‘E’ is the potential.

The term overpotential $\eta$ is dependent on the rate of exchange of electrons at the interface under reversible conditions and the Tafel slope ‘b’ is dependent on the reaction mechanism:

$$\eta = b \log \left( \frac{i}{i_o} \right)$$  \hspace{1cm} (2.18)

where ‘i’ is the current density and ‘$i_o$’ is the exchange current density. One of the ways of lowering the energy consumption is to reduce the anodic overpotential in the electrolysis process. Several materials (Smolinka 2009) have been studied as electro catalysts for the OER.

2.4 ELECTRODEPOSITION

One method of fabricating pure metal and alloy coatings is by electrodeposition. It has been employed as a metallisation technique for near to two centuries, mainly as a means of coating metals/alloys on other metals to protect against corrosion and also to achieve better performance. Electrodeposition is often also called ‘Electroplating’, a short version of “electrolytic deposition”, and the two terms are used interchangeably (Barrera et al 2000). It refers to a layer growth phenomenon which consists of the formation of a metallic coating onto a base material through the electrochemical reduction of metal ions from an electrolyte. This process consists essentially of the immersion of the metal to be coated and the counter electrode in a vessel containing the electrolyte followed by the connection of the two electrodes to an external power supply to make current flow possible (Fezani et al 2013; Aerts et al 2007). This method is very flexible in the choice of materials that can be used because numerous metals, alloys,
semiconductors, and oxides can be deposited from the bath solution that can be aqueous or non-aqueous, under the conditions that are compatible with the template.

The reduction of metal ions $M^{n+}$ in aqueous solution is represented by:

$$M^{n+} \text{(solution)} + n \, e^- \rightarrow M \, e$$

(2.19)

It can be achieved by means of two different processes: (i) an electrodeposition process in which $n$ number of electrons is provided by an external power supply and (ii) an electroless deposition process in which a reducing agent in the solution is the electron source, which involves no external power supply. The electrolyte is an ionic conductor where chemical species containing the metal of solutions are dissolved into a suitable solvent to form a molten salt (Hall 1985).

The electrochemical deposition, is governed by two laws namely Faraday’s law (Equation 2.20) and the Nernst equation (Equation 2.21). Faraday’s law is used to calculate the amount of substance deposited during the process and the Nernst equation is used to determine the theoretical potential for electrochemical reactions to take place (Sadovnikva & Belikov 1978)

$$w = \frac{I \cdot t \cdot M}{z \cdot F}$$

(2.20)

$$E = E_0 + \frac{RT}{nF} \ln \left( \frac{C_R}{C_O} \right)$$

(2.21)

where $w$ is the weight of the deposited material in grams (g), $I$ is the measured current in amperes, $t$ is the time for which the current has been supplied in seconds, $M$ is the molecular weight in grams per mole (g/mol), $n$ is the unit-
less valence of the deposited atoms, $F$ is Faraday’s constant which is $9.64853 \times 10^4$ C/mol, $E$ is the cell potential in volts, $E_o$ is the standard cell potential at 298 K and 1 atm. in volts (V), $R$ is the gas constant which is 8.3145 J/mol·K, $T$ is the temperature of the process in Kelvin (K), $C_R$ is the total concentration of the reactants or oxidants, products $C_O$ is the total concentration of the products or reductant.

Four types of fundamental knowledge are involved in the process represented by Equation (2.19): (i) Metal-solution interface as the locus of the deposition process: In this process, there will be an exchange of metal ions $M^{+}$ between the metal $M$ and the aqueous solution of its salt, $(MS)$ into which it is immersed. In response to the charging of the metal side of the interface (Chen et al 2002), there is a rearrangement of charges on the solution side of the interface. (ii) Nucleation and growth processes of the metal lattice $M$ (lattice): In this process two basic approaches are involved: (a) the arrival and adsorption of ions at the surface, and (b) the motion of these adsorbed on the surface. (iii) Kinetics and mechanism of the deposition process: In this case the charge-transfer reaction is the rate determining step and the substances formed during the electrode reaction are transported from the bulk solution to the interface and from the interface to the bulk solution (iv) Structure and properties of the deposits: The parameters are current density, electrode potential, solution temperature, pH, concentration of reacting species, substrate and processes such as hydrogen evolution or oxygen evolution may influence the deposits (Alwitt & McClung 1993). The material and the surface finish of the substrate also influence the deposition process as the nucleation rate on the substrate differs from that on the freshly plated deposits (Panek & Budniok 2008).

During electroplating, the number of metal ions in the electrolyte is always maintained at equilibrium. If the anode is fabricated from other
elements such as inert metals, then the oxygen (O₂) gas evolved at the anode decreases the number of metal ions in the electrolyte. Such a cell requires more maintenance as new metal salts must be added frequently (Hayashi & Furuya 2004). Secondary reactions such as hydrogen evolution can take place at the cathode. These reactions will lower the efficiency of the cell and change the pH value unless a buffer is added to the electrolyte to stabilize the pH.

The current distribution on the cathode is given by two contributions:

**Primary Current Distribution**

It depends on the resistivity of the electrolyte and the anode/cathode/cell geometry. The primary distribution can in principle be calculated using standard electrostatic theory. The current density will be higher in areas with protrusions and low density of structures, compared to areas with cavities and high density of structures (Mohamed et al 2014). Placement of dummy structures in areas with small and isolated structures, can improve the uniformity significantly.

**Secondary Current Distribution:**

Due to the complex relation between different over-voltages and the current, the primary current distribution is changed in a manner that is difficult to predict. As an example, diffusion through the boundary around the sample can increase the theft fields and thus plating current, which leads to some in homogeneities around the plated areas (Petri & Tsirlina 1994). This limits the plating current densities, as higher current densities leads to a higher diffusion over-voltage or fields (Conway 1982). However, this defect may be overcome by control of plating parameters such as stirring, plating temperature and current density.
2.5 NICKEL ELECTRODEPOSITION

Nickel electroplating is a well-known process that has been used in industry for a long time (Miles et al 1976). Electroplating may be carried out using different types of electrolytes to obtain smooth, stress-free deposits with homogeneous material distribution at high deposition rates (Sheela et al 2002; Adelkhani & Arshadi 2009). Electro deposited nickel is a low cost electro catalyst that is known to be highly active and resistant to corrosion for use in alkaline water electrolysis applications. The physical and chemical properties of the electro deposited nickel in micro (or) bulk form; its electrochemical properties have been well investigated. The thickness and volume of the plated nickel can be easily changed as per requirement. Further, nickel is one of the metals that have been considered for both hydrogen and oxygen evolution reactions (Wiesener & Ohms 1990).

The electrodeposition reaction of nickel in its simplest form can be represented as:

\[ \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0 \]  

(2.22)

when nickel salts are dissolved in solution, the nickel is present in solution as divalent \( \text{Ni}^{2+} \) ions. When current flows these divalent nickel ions are converted to metallic nickel (\( \text{Ni}^0 \)) at the cathode. As the nickel ions discharged at the cathode are replenished by the nickel ions formed at the anode, the nickel plating process can be operated for long periods of time without interruption (Wood 1986). A method to improve the catalytic property of nickel is to modify the coating technique to obtain coated surfaces with high electrochemical activity (Yamaguchi et al 1995). Therefore it will increase the deposition rate of the plating process.
2.5.1 Conditions Affecting the Properties of Ni Electrodeposition

The characteristics of electrodeposited metals and metal alloys are mainly influenced by the environment in the immediate locality of the electrode. The rate of formation of the nuclei by the discharge of the ions at the cathode and the rate at which these nuclei grow into large crystals influence the smoothness and hardness of the deposit (Hasan et al 2003). There are many factors that influence the Nickel electroplating namely,

- Bath concentration
- Current density
- Temperature
- pH
- Impurities
- Coating thickness

2.5.2 Bath Concentration

Under normal plating conditions, the increase of bath concentration increases the concentration of metal ions in solution. Therefore it will increase the deposition rate of the plating process. Uniformity of electrodeposition is influenced by the bath concentration as it influences the uniformity of current distribution. Thus the optimum bath concentration is required for uniformity of the deposit.

2.5.3 Current Density

The plating current density plays a significant role in electrodeposition. At low current densities the rate of discharge of ions takes place at a slow rate, which allows copious amount of nuclei formation. The
formation of fresh nuclei is always essential. The deposit obtained under this condition is of coarse crystalline structure. As the current density increases, the discharge rate of the ions also increases, and fresh nuclei will be formed (Mao et al 2011). The resulting deposits will consist of smaller crystal size. Thus, the increase in current density, within optimum limits affords more fine grained deposits. Crystals at high current densities tend to grow out from the cathode compartment towards regions where the solution is more concentrated hence creating fresh nuclei in the deposits.

2.5.4 Temperature

Increasing the temperature of the plating bath appears affect the plating process in two ways. On one hand, it promotes the diffusion of ions to the cathodic compartment which leads to roughness in the deposits (Mansfield 1979) and on the other hand, it also increases the rate of growth of the crystal nuclei, so that the deposit will have a tendency to be of coarse nature. When operating at moderate temperatures, such as those generally applied to electroplated nickel, the first of the above mentioned effect predominates, thus the deposits with improved roughness are obtained. But at high temperatures the quality of the deposit decreases.

2.5.5 pH

The pH of the solution influences the rate of discharge of hydrogen ions, thus causing the solution in the cathode layer to become alkaline and precipitate as hydroxides. The presence of a significant amount of these compounds will make the resulting deposit demonstrate fine grain morphology. In addition hydrogen evolutions are often accompanied by the formation of streaks in the deposits (Li et al 2011a). A small quantity of acid or base is added to maintain the pH of nickel electrodeposition bath during direct current electroplating operations.
2.5.6 Impurities

Electroplated films normally contain various types of impurities. The source of these impurities may be from the added chemicals, added particles, cathodic products, hydroxides and bubbles. The effect of a particular additive is specific for a given metal (Bronoel & Reby 1980). An excessive amount of additive in the electrolyte can cause the deposit to become brittle and break apart at the crystal interface, where there is a relatively thick layer of the added substance. Hydrogen, oxygen, carbon, sulphur and chloride are the most common impurities present in nickel deposits that adversely influence the physical properties (Dai et al 2008).

2.5.7 Estimation of Coating Thickness

The amount of nickel that is deposited at the cathode is calculated by the product of the current and the time. If the area being plated is known, the average nickel coating thickness can be estimated. Thickness equals the weight of nickel divided by the product of the area and the density of nickel (8912 kg/m$^3$). As a small percentage of the current is consumed at the cathode while discharging hydrogen ions, the efficiency of nickel deposition is normally less than 100%. Nickel-ion concentration and pH will change as the bath is used (Chen et al 2007). The pH of the solution is normally maintained by adding acid.

2.6 Nickel Distribution

It is desirable to coat uniform thicknesses of nickel to all surfaces to achieve predictable long life and to meet coating specifications that require minimum coating thickness ranges at specified points on the surface. The amount of the deposit on the surface of any object being plated is proportional to the quantity of current that passes the surface (Chang et al 2009). Some
areas on the surface require less current, because the electric field is highest at the surface with the smaller curvatures (Tasic et al 2011). The current and the rate of metal deposition in the curvatures are lower than surfaces that project from the surface.

2.6.1 Process

The basic constituents of the nickel plating bath known as Watts solution and operating parameters are given in Table 2.1. Nickel sulphate, nickel chloride, and boric acid serve the same purposes as they do in the Watts solution (Table 2.1).

Table 2.1 Nickel electroplating-Watts bath

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (II) sulfate</td>
<td>250</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>45</td>
</tr>
<tr>
<td>Boric acid</td>
<td>36</td>
</tr>
<tr>
<td>pH</td>
<td>3-6</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>50°C</td>
</tr>
<tr>
<td>Current density</td>
<td>3-10 A/dm²</td>
</tr>
</tbody>
</table>

Nickel sulphate is the principal source of nickel ions. It provides most of the nickel ion required with stable anions that are neither reduced at the cathode nor oxidized at the anode (Navarro et al 2005). Nickel chloride improves anodic dissolution increases solution conductivity and improves bath efficiency (Krstaji et al 2008). It also introduces chloride ions that are required to prevent anode passivation. Boric acid serves to produce smoother and ductile deposits (Kaninski et al 2009). Wetting agents are required to reduce the pitting due to the binding of hydrogen bubbles that are formed
during the deposition process. The schematic view of direct current electrodeposition of nickel is shown in Figure 2.3.

![Schematic view of direct current electrodeposition of nickel](image)

**Figure 2.3** The schematic view of direct current electrodeposition of nickel

### 2.6.2 Electrochemical Characterization Methods of Ni Electrodeposition

Electrochemical methods cover a wide range of analytical techniques with the fundamental signal measured being electrical in nature (current or voltage) resulting from redox reactions (Veziroglu & Barbir 1992). Like other analytical techniques, electrochemical methods yield both quantitative and qualitative information. In addition, some electrochemical methods will give information about non-redox chemical processes occurring before or after redox reaction.
The rate of charge transfer can occur homogeneously in solutions and heterogeneously on electrode surfaces. For a heterogeneous reaction, either oxidation or reduction of electrons transferred from one species to others takes place in the electrode. This is a surface phenomenon and the electro active species in the solution has to be transferred to the electrode surface (Zeng & Zhang 2010). Therefore, in a solution state, the concentration of species at the electrode surface depends on the mass transport of these species present in the bulk solution. If the kinetics of the electrode reaction is much faster than this transport, the reaction is reversible (Lasia & Rami 1990). Cyclic voltammetry, Potentiostatic experiments are the Faradaic techniques used. The electrochemical methods are extremely useful for the characterisation of nickel structures and for their synthesis (Schlesinger 2004).

2.6.3 **Cyclic Voltammetry Studies**

In cyclic voltammetry (CV) measurements, a triangular potential waveform is applied to the electrode and the corresponding current is recorded. This technique has been widely applied in the studies of the electrochemistry of interface species and in the study of electrochemical reactions with subsequent chemical reaction steps. It also shows the wide range of potential which the solvent is stable and the degree of reversibility of the electrode system (Chen & Lasia 1992). A continuously time varying potential is applied to the working electrode. It is also useful for studying electrochemical cell performances. It enables independent estimation of oxidation as well as reduction reaction potentials and throws light on their mechanism. The potential sweep technique is normally used at stationary electrodes. Moreover, within certain limitations, it enables estimations to be made of various parameters such as double layer capacitance, columbic efficiency, and reversible potential.
The electrode is subjected to continuous change in the potential both in the forward and reverse direction in a cyclic manner. The important parameters that are needed to run a CV experiment are:

- Initial potential, \( E_i \)
- Initial sweep direction, (+ve or –ve)
- Sweep rate, (mV/s)
- The maximum potential, \( E_{\text{max}} \)
- The final potential, \( E_f \)

The real power of this technique lies in its ability to investigate mechanisms and potentials of electrode system (Marozzi & Chialvo 2000). It may also be used to show the ability of the deposits to store charge and to respond to the applied potential. When the areas under the oxidation and reduction peaks are approximately equal the process demonstrates the electrochemical reversibility and efficiency of the redox process.

### 2.6.4 Potentiodynamic Studies

Potentiodynamic studies involves the monitoring of the resulting current (I) as a function of applied potential (E) to give the I-E curve over a wide range of potential. The potential is stepped from an initial value that causes no current to flow to a potential that causes current to flow. Because the experiment is diffusion controlled step after a certain time almost all molecules that are able to reach the electrode are reduced. Typically, a three electrode potentiostat system is used: a working electrode, reference electrode and a counter electrode. The potential is controlled between the reference electrode and the working electrode. The current flows between the working electrode and the counter electrode. However, if the potential is scanned too
far in a particular direction, which are defined irreversible, peaks develop corresponding to a loss in redox reversibility of the deposits.

### 2.6.5 Effects of Nickel ion Concentration

The high nickel concentration improves the so-called ‘micro-throwing’ power of the watts bath, meaning structures with small dimensions are filled at a similar rate as those with larger cross sections (Marozzi & Chialvo 2001). This avoids the use of leveling agents which are usually added to improve the uniformity of the metal deposition (Damian & Omanovic 2006). Boric acid is used as a buffer, controlling the pH. Sodium lauryl sulfate is added for two purposes: i) as an anti-pitting agent and ii) as a wetting agent. Anti-pitting agents are necessary to promote release of hydrogen gas bubbles formed at cathode by discharge of hydrogen ions clinging to the cathode surface producing pits. The wetting agent is used to suppress pit formation on the surface of the plated structures. The wetting agent also reduces the surface tension of a liquid, thereby causing the penetration of the electrolyte into the deep and narrow trenches, so that the electroplating deposits metal evenly on the metallic base of the patterned areas of the resist.

Organic additives such as: 1) Saccharine or Thiourea, 2) Coumarin, and 3) Sodium lauryl sulfate are often added to the plating bath. Saccharine and Coumarin are both used as brighteners and stress reducers. Stress can be caused by the incorporation of foreign materials in the electrolytes such as co-deposited hydrogen which obstruct normal lattice formation and produces lattice mismatch (Ivy 2004). Saccharine works as a stress reliever by infiltrating the structure of deposited nickel and altering the contraction of the lattice as the ions arrange themselves in regular lattice positions. However, if the organic additives exceed a specific concentration, they can induce compressive stress. These additives also diminish nickel grain size, improving
the hardness of the plated structures (Divisek et al 1994). Electroplating may be carried out by i) Direct current electrodeposition ii) Pulse electrodeposition.

2.7 PULSE ELECTRODEPOSITION

In pulse electro deposition the potential or current is alternated swiftly between two different values. This results in a series of pulses of equal amplitude, duration and polarity, separated by zero current (Kashi et al 2011). Each pulse consists of an on-time ($T_{on}$) during which potential and current is applied, and an off-time ($T_{off}$) during which zero current is applied as shown in Figure 2.4. The duty cycle is given by

\[
\text{Duty cycle} = \frac{\text{on time}}{\text{on time} + \text{off time}} \times 100
\]  

(2.23)

![Figure 2.4 Waveform of pulse current](image)

Pulse plating has emerged as a novel technique for deposition of metals and alloys. In the conventional direct current electrodeposition, there is only one parameter, namely the current density, which can be varied. But in pulse methods we have three variables that are of primary importance. They are (1) peak current density, $i_p$ (2) current ‘on’ time and (3) current ‘off’ time. The sum of ‘on’ and ‘off’ times constitute one pulse cycle. Some important relationships used in pulse plating are as follows:
Average current density, \( i_a = i_p \times \text{duty cycle} \). The average current density is similar to that used in d.c. electroplating. Duty cycles may vary from 1 to 100\% and on-off times from microseconds to milliseconds. So, in pulse plating we have an unlimited number of combinations of different pulse current densities for obtaining a given average current density (Kanani 2004).

During \( T_{\text{off}} \) time, the ions migrate to the depleted areas. Hence, ions are more uniformly distributed for deposition onto the part when \( T_{\text{on}} \) pulse occurs (Ayyadurai et al 2007). Thus the electrical double layer which is formed around the cathode discharges during the off time resulting in the passage of ions through the double layer on cathode surface. In direct electrodeposition, this double layer obstructs the ions from reaching the cathode surface (Lowenheim 1997). The schematic view of pulse electrodeposition of nickel is shown in Figure 2.5.

![Figure 2.5 The schematic view of pulse electrodeposition of nickel](image-url)
Compared with direct current electrodeposition, pulse electrodeposition can improve uniformity of the layer and better current distribution. It overcomes the shortages of single direction and persistence of direct current by means of utilizing the relaxation of pulse current. Therefore, it is more favourable for metal alloy coatings and has attracted a great deal of attention (Zoikis et al 2010). The pulse plating yields a finer grained deposit as the pulse current density is considerably higher than the corresponding direct current density. It has been established that pulse current densities have beneficial effect on the properties of electrodeposits (Ganesan et al 2006; Boonyongmaneerat et al 2010; Xu et al 2010) Pulse electrodeposition of metals and alloys has been investigated by Adelkhani & Arshadi (2009) and the results show that pulse electrodeposition is a suitable technique to produce the alloy with controlled composition and improved microstructure of the coating. In addition pulse plating has been identified as a means to lower residual stress, avoid incorporation of other bath components and to control the deposit composition and morphology (Hou et al 2007). Pulse electrodeposition also gives higher rate of deposition and improved physical and mechanical properties (Xu et al 2008; Schlesinger 2004).

2.8 SONO ASSISTED ELECTRODEPOSITION

Over the past few years the use of power ultrasound has found wide applications in the chemical and processing industries where it is used to enhance both sequential growth and acoustic cavitation. Ultrasonic agitation during electroplating is known to improve the nature of the deposit obtained. An investigation to look into the beneficial effects on the deposited metal (Guo et al 2011; Balachandran et al 2009; Prasad et al 1993; Xia et al 2010) showed that the micro hardness of the electroplated nickel alloy increased when plated in ultrasonic field. Further, the ultrasound assists in the formation of molecular hydrogen, which leaves the surface as bubbles.
This form of agitation also prevents impurity particles from remaining on the surface. When ultrasonic waves are passed through the electrolyte solution, bubbles are formed which grow and collapse due to continuous absorption of energy from alternating compression and expansion cycles of the sound waves.

Thus regions of high porosity were obtained. The ultrasonic agitation of the plating bath increased surface smoothness and decreased the residual stresses. Moreover the use of ultrasonic waves not only for improves the coating surface but also decreases the coating time due to higher plating current.

Furthermore the surface of a substrate has small areas with the property of initiating pores which are referred to as precursors. These precursors prevent fusion of crystals and as the coating thickens a pore is generated. Inclusions of oxides, polishing abrasive, sulphides and dirt particles settling on the substrate from the plating solution, are pore precursors. (Banks & Compton 2003)

![Figure 2.6 The schematic view of sono assisted electrodeposition of nickel](image)
Another significant aspect is that porous electrodes with an appropriately adjusted pore allow easy release of the evolved oxygen and is therefore important for establishing relatively low true current densities in the anode and correspondingly low overpotential which render the necessary longevity to the electro catalyst (Mallik & Ray 2011). The schematic view of sono assisted electrodeposition of nickel is shown in Figure 2.6.

It is therefore imperative that such highly porous coatings for hydrogen evolving cathodes be structured and divided up by coarser cracks, channels or coarser pores (Kibria & Tarafdar 2002). Simultaneously these cracks, being at least temporarily filled with electrolyte, allow a greater penetration depth for the current into the catalyst layer and further allow a convective, bubble driven exchange of the electrolyte and fast supply of water.

2.9 PULSE-ULTRASONICATION ELECTRODEPOSITION

Pulse-sono platings form more compact layers with less stress in the surface of the coating than that of pulse platings. Hence, the coatings which are developed on pulse-sono platings are expected to exhibit more stable form over other plating techniques (Kabat & Heffel 2002). In recent years, the demand for coated surface with low surface roughness has increased as these could lead to a decrease in the film resistivity. It was also reported (Reisse et al 1994) that ultrasonic treatment during film deposition could improve film uniformity. Thus in the pulse electrodeposition with ultrasonication, the rate of film deposition is also increased, compared to the case without ultrasonic influence. Pulse electrodeposition with ultrasonication could affect the reaction kinetics in two ways (i) there is a sharp change in the current density at both the beginning and end of a pulse that would cause changes in the state of electrical double layer (Ursúa et al 2009). (ii) in the presence ultrasonication, the metal ions were vibrating and resulting in a
change in the surface concentration of the metal ion influences the kinetics and the structural aspects of the deposition process. The mass transport effect increases since ultrasonication reduces the resistance of the double layer barrier (Van et al 2009). The schematic view of pulse-sono assisted electrodeposition of nickel is shown in Figure 2.7.

![Figure 2.7 The schematic view of Pulse-Sono assisted electrodeposition of nickel](image)

The aim of this technique is to improve more fine grains and uniform deposition for Ni-based alloys and study their electrochemical behaviour in alkaline solution in an electrolysis mode.

In general, when oxygen evolution takes place on a metallic electrode, the surface is already covered with appropriate oxides layer. Moreover, This transformation in the oxidation state of nickel has been
observed to occur in cases where Ni (II) oxide has been formed once and has been electrochemically oxidised to Ni (III) oxide. It should also be pointed out that in order to improve the usage of these materials; various methods of their modifications could be applied (Li et al 2011b). It is possible to introduce metals in ease of pulse plating and ultrasonication bath of their particles. Such limiting are often carried out to obtain electrodes with very developed, rough and uniform surface. (Socol et al 2002).

2.10 ALLOY ELECTRODEPOSITION

Alloys find very wide applications since their properties are often superior to those of pure metals. Alloy coating show superior properties in terms of corrosion resistance, hardness, density, substrate protection, toughness, strength, and wear resistance. Hence it is well proved that the alloy deposition provides properties not attainable by electrodeposition of individual metals (Langer et al 2007; Jaksic 1986). Electrodeposited alloys may have the same phase structure as those formed metallurgically. By using specific metal combinations, electrodeposited alloys can be made to exhibit hardening as a result of heat treatment subsequent to deposition (Chen et al 2009).

Previous studies have shown that binary alloys such as Ni-Fe, Ni-Co, Ni-Bi, Ni-Zn (Han et al 2010; Jaksic et al 2000; Rodriguez et al 2004; Stojic et al 2006; Solmaz et al 2008; Cardona et al 2011) show an increase in the catalytic activity in the OER and have comparable kinetic parameters to that of the noble metals (Pt, Ru, Pd). This increase has been assigned to the synergetic characteristics of the elements forming the alloy and to the electrode surface area increase (Solmaz et al 2011; Doner et al 2012). Further studies have shown that addition of sulphur in the alloy helps in activation of gas evolution so that the resistance offered due to the adherence of the
bubbles on the electrode decreases (Chi et al 2005; Chun et al 2009; Ohmori et al 2001).

Incorporation of zinc increases surface area and catalytic activity and has lower over voltage and the presence of sulphur increases the rate of detachment of gas bubbles from the electrode surface and it decreases the cathodic over- voltage, thus increasing the current density (Wolf et al 1981; Ananth & Parthasaradhy 1997; Crnkovic et al 2004; Saravanan & Mohan 2011). Furthermore the use of sonication furnishes an increased mass transport limit and increase the smoothness of the deposited layer compared to that of pulse plating. Hence the combination of pulse plating with sonication improves the uniformity of the layers and current distribution.

Dutta (1990) have carried out Ni-Zn-S deposition by different methods, such as Normal (direct current) electrodeposition, Pulse electrodeposition and Normal electrodeposition with ultrasonication and Pulse electrodeposition with ultrasonication on nickel mesh that have been pre- treated in a variety of ways to maximise their performance as anode materials in strong basic media. In order to investigate the catalytic activity of the prepared layers, Tafel linear polarization measurements were performed, and the corresponding electrochemical parameters like the Tafel slope, exchange current density were derived from the recorded curves.

\[
\eta = a + b \log j \tag{2.24}
\]

where \(\eta\) (V) represents the overpotential, \(j\) (A/cm\(^2\)) the resulting current density, \(b\) (V/ decade) the Tafel slope and \(a\) (V) is the intercept related to the exchange current density \(i_o\) (A/cm\(^2\)) through Equation:

\[
a = 2.303 \frac{RT}{(1-\beta)} nF \log j_o \tag{2.25}
\]
The other parameter of interest is $b$, can be calculated from the Tafel slope as:

$$b = \frac{2.303RT}{(1-\beta)} nF$$

(2.26)

where

$$\beta = 1-2.303 \frac{RT}{b} nF$$

(2.27)

where ‘$n$’ represents the number of electrons exchanged, $F$ (96,485 $C/mol$) is the Faraday constant, and $R$ (8.314 $J/mol K$) is the gas constant.

### 2.11 COMPLEXING AGENT

The importance of additives such as boric acid, citric acid and ascorbic acids influencing the electrodeposition of Nickel alloys were described by Kieling (1997). It was shown that complexing agents influence the kinetics of electrodeposition, and the morphology of the Ni powders. It was also found that finer powders were produced in the presence of citric acid in comparison with those obtained in the presence of oxalic acid (Nikolic et al 2010). The study on effect of organic additive, tri sodium citrate (Miulovic et al 2012; Seghiover et al 1998) as stabilizing agent reveals that the organic additives have been used for structure related factors to control the nucleation, growth and alignment of crystal phases.

Miulovic et al 2012 present a report on the improved efficiency of alkaline electrolytic production of hydrogen by in situ addition of cobalt and chrome based ionic activators directly into the electrolyte during the electrolytic process. During electrolysis process the ionic activators deposit metal particles on the surface of the Ni cathode electrode and form an active, porous structure of high surface area. This simple process of adding in situ activating compounds directly into electrolyser reduces the energy requirements per mass unit of hydrogen produced by about 15%, compared to non-activated system, for a wide range current densities and temperature.
Energy saving is higher when the temperature of operation is high and on at higher current densities. Structural and morphological characteristic of deposit formed on the cathode during the electrolytic process after in situ addition of activators, reveal interesting electrode surface pattern with highly developed surface area and uniform distribution of the pores. The deposit obtained also exhibits long term stability.

In order to improve efficiency of the electrolytic process it is necessary to add complexing agent into the electrolytic solution. The presence of complexing agents in the electrolytic solution is found to improve the life time of the electrodes as well as create more organized transfer channels and also reduce surface tension of the electrolyte. If the surface tension of the electrolyte was reduced, then the bubble can leave the system easier. With the introduction of complexing agent in the electrolytic system, the overall efficiency increases, with decreases the over voltage drastically. The significant increase in current density should be due to the competitive adsorption of metal ion species with complexing agent on the surface. Optimum concentration of the complexing agent/ionic activator has to be identified for improvement in the properties.

In general, with an increase in electrolyte concentration, the surface charge will be compensated at a lower distance from the particle surface, which means the potential drops faster and the diffuse layer becomes thinner (Lyons & Brandon 2008; Elumalai et al 2002). Hence the role of suitable complexing agent adsorbs with the negatively charged part of the molecule onto the particle surface and forms the inner Helmholtz layer (Krstajic et al 1997, 2001). Adsorption takes place according to the theory of adsorption isotherms. Accordingly the potential of the inner Helmholtz layer increases with the increasing surface coverage, leading subsequently to an increase of the zeta potential and an increase in the physical stability of the suspensions.
(Oguzie et al 2007). At high complexing agent concentrations, well above of the plateau of the adsorption isotherm, electrolyte stabilisers can cause a decrease in the diffuse layer leading to a decreased zeta potential and a decreased physical stability (Jaksic 2000). Therefore it is important to find the optimum concentration for a complexing agent.

2.12 STABILIZERS

Recently, Nikolic et al (2010) have shown that alkaline electrolytic hydrogen production can be made efficient by the addition of activating compounds in the ionic and complex form. Sodium tungstate and tris (ethylene diamine) Co (II) chloride were added as ionic activators into the electrolyte (6M KOH) during electrolytic process. A reduction of 15% in the energy consumption was obtained compared to the non-activated system. Addition of ionic activators leads to increase in surface area, porosity and performance improvement due to the synergistic effect of the metal on the surface of the electrode. The effect of ionic activators and complexes in alkaline water electrolysis has been emphasized by improved performance in the presence of molybdate, chromate and cobalt based compounds (Bocutti et al 2000; Trasatti 2009; Stojic et al 2003).

The instability of the electrolyte due to Ni oxidation and hydroxide precipitation is one of the problems preventing formation good coating during Ni plating. One method to reduce the precipitation in the electrolyte solution is the addition of small quantities of stabilizing agent such as citric acid to the alkaline solutions used as the ability of Ni to form complexes with Ni is very well established (Thomas & Thomas 1997). It was observed that stabilizing agents influence the kinetics of electrolysis by reducing the surface tension of the solution, so that the oxygen gas generated at the anode was easy to leave the surface of anode (Kaninski et al 2004). Citric acid (CA) is also used as a chelating agent to control the deposition rate of metals in electroplating and
electroless plating operations. It is also used to buffer the pH of the plating bath. The effects of additives in the electroless Nickel deposition process have been studied by electrochemical analysis. (Hasan et al 2003; Jaksic 2001)

Addition of CA to the electrolyte stabilizes Ni at intermediate pH in basic solutions. It facilitates the formation of NiOOH / Ni (OH)$_2$ couple, an active redox pair for the anodic reactions (Marceta et al 2011). The use of citrate as a complexing agent in electroless nickel deposition prepares coating of high quality at high deposition rate. The major advantages of using citrate as a complexing agent in nickel plating’s are:

- Separation of precipitate in plating bath,
- Avoid the amount of precipitation of Ni (II) in citrate bath solutions.
- Separation of Ni (OH)$_2$ precipitate
- Leaching of Ni (II)-citrate complex from precipitate using sulphuric acid.

Thus literature studies have proven that addition of activators/complexes improve the efficiency of the system.

2.13 MEMBRANE ELECTRODE ASSEMBLY

The Membrane Electrode Assembly (MEA) consisting of anode and cathode electrodes coated with electro catalyst and pressed on the either side of the membrane is considered as the heart of an energy system that drives the electrochemical process (Wang et al 2013a). Catalyst coating on electrodes may be achieved by different techniques such as impregnation reduction method, brush coating methods, spraying techniques etc. It was proposed to evaluate the effect of various coating techniques on the
performance of the composite membranes. Platinum coated cathodes were prepared by non-equilibrium Impregnation-Reduction (I-R) method and conventional brush coating method as Platinum is the most active catalyst for HER. Iridium oxide based catalysts were used for anode as they exhibit Since \( \text{IrO}_2 \) (Fujiwara et al 2002; Kauffman et al 2011) catalyst exhibits high corrosion resistant properties but slightly lower electro catalytic activity than \( \text{RuO}_2 \) (Goodenough et al 1989). All coating methods were carried out mechanically. Hence it is essential to evaluate the performance of the MEAs in various circumstances.

2.13.1 **Electrodes**

In general, all electrochemical reactions are governed by mass transfer limitations which occur only at higher operating current densities. These reactions take place on the electrode surfaces. To activate the cell reactions, electrodes contain catalyst particles. Furthermore it needs to be operated at moderate temperature and choice of pH range makes more adherences to the surface.

The electrodes in electrolysers should: i) provide a good conductive pathway ii) provide many active sites for the reactions to take place iii) offer least resistance to flow of ions, electrons and products. To provide physical barrier that separates the bulk gas phase and the electrolyte. The electrodes also must be porous in nature, so that both electrolyte and gases should not be mix with each other.

2.13.1.1 **Electrocatalyst**

Platinum (Pt) is long known to be the best cathode catalyst for water electrolysis due to its high surface area, moderate strength of adsorption and also has the lowest over potential of all metals. From the view of volcano
plot, we can observe the Pt having the highest values (Jaksic et al 2001). The enthalpy of formation of higher valent from lower valent oxide should be average and not too low. The rate of the cathode catalyst depends upon the overvoltage, \((\eta)\) depends in turn upon the value of the over potential, its surface state, and the conditions under which the electrolysis process is carried out.

These conditions includes: both concentration and temperature of the electrolyte, need be taken into account, However due to its high cost, and the favoured operation of the PEM electrolyser at high current densities, clever ways have been prepared to deposit fine Pt particles either on the electrode support plate, or directly onto the membrane, which is then clamped for good electrical continuity. Iridium oxide (IrO\(_2\)) is the best anode catalyst for PEM electrolysers (Baglio et al 2011). The electro catalysts that are formed as nanocrystallites by chemical reduction method of adding precursors to form colloids that are harvested and heat treated at optimum temperature to become a stable oxide. Moreover the anode catalyst is the main factor related to energy efficiency. The mechanism for oxygen evolution reaction can be written as:

\[
2\text{H}_2\text{O} \rightarrow 2\text{OH}_{\text{ads}} + 2\text{H}^+ + 2\text{e}^- \quad (2.28)
\]

\[
4\text{OH}_{\text{ads}} \rightarrow 2\text{H}_2\text{O} + 2\text{O}_{\text{ads}} \quad (2.29)
\]

\[
2\text{O}_{\text{ads}} \rightarrow \text{O}_2 \quad (2.30)
\]

\[
\text{O}_2 + 2\text{H}^++2\text{e}^- \rightarrow \text{H}_2\text{O} \quad (2.31)
\]

For instance Datta et al (2013) found that the performance and long-term stability of a water electrolysis pilot plant could be enhanced when IrO\(_2\) electrodes were hot-pressed on both sides of a Nafion\textsuperscript{®} membrane in comparison with Pt electrodes, and they obtained lower anodic overvoltage and a better long-term stability of the cell voltage.
The theory of the process mechanisms involved at the oxygen catalyst is less well understood than for hydrogen catalyst because of the difficulties introduced by the participation of the anode catalyst itself in the electrolysis process. The most possible discharge step involves the formation of oxygen atoms adsorbed on a metal atom covered with strongly bound oxygen atoms, the reaction as follows:

\[ \text{MO} + \text{OH} \rightarrow \text{MO} - \text{O} + \text{H}^+ + 2\text{e}^- \]  

(2.32)

where MO-O represents an oxygen atom lightly adsorbed on an oxidized surface of the metal ‘M’. Hence in order to minimize the overpotential requires maximizing the oxygen evolution catalyst area available for the reaction. The chemical processes that contribute to the activation loss involves in the process of the adsorption of reactant species, electrons transfer across the double layer of an electrolyzer, desorption of a product species, and the nature of the electrode surface. (Bard and Faulkner, 2001)

Thus the effects of catalyst preparation and dispersion on activity are among the major consequences that need to be addressed for improving the overall performance, so that an optimum compromise is achieved between performance and cost. A significant ohmic, activation and transport loss is accredited to the dispersion of the anode catalyst. A good contact between the catalyst and the membrane is essential in order to minimize the ohmic losses and contact between the MEA and electrolyte is a necessity for proton transport to the catalyst particles.

### 2.13.2 Bipolar Plates

Bipolar plates are also known as flow field plates which function to separate the reactants of adjacent unit cells. Hence the cells are connected in series, and hydrogen is produced on one side of the cell, oxygen on the other
side of the cell. They also serve as current collectors and form the supporting structure of the stack cell. In water electrolysis, the titanium is used for the fabrication of bipolar plates. One face of a bipolar plate forms the anode compartment of unit cells and the other side is the cathode compartment of the adjacent unit (Häussinger et al 2000). The total voltage of a stack is determined by the number of individual cells and the current by the active area of the unit cells. The materials for bipolar plate should have good electric and thermal conductivity, sufficient mechanical strength and chemical stability in both oxidizing and reducing conditions (Barbir 2005b).

2.13.3 Membrane

Membrane played an important role in MEA, where it functions as a separator to prevent the mixing of gases and as a solid electrolyte for transporting protons from anode to cathode. To achieve high efficiency the membrane must possess the following properties:

- High proton conductivity.
- Good mechanical strength and stability in operating conditions.
- Good chemical and electrochemical stability.
- High mobility to maintain uniform electrolyte content and prevent localized drying.
- Low cost.

The polymer electrolyte membranes are an ion exchange material, which usually consist of a polymer based backbone which sulfonic acid groups are attached. These negative ions are fixed form of the polymer and cannot move, but the protons of the acid groups (positive ions) are free to migrate through membrane.
The first application of proton conducting membranes was in NASA’s space centre. A partially sulfonated polystyrene sulfonic acid membrane developed by General Electric was utilized in Gemini spacecrafts. However, this type of membranes exhibited brittleness in the dry state (Bockris & Srinivasan, 1969). In terms of polymeric membrane (Sourirajan 1964) most of the literature especially on proton exchange membranes (PEM) is based on Nafion® in spite of its high cost and limited range of temperature of operation (Hobson et al 2001; Millet et al 1996).

There have been persistent attempts in literature to develop alternate membranes to perfluoro sulphonic acid based membranes. However many of these attempts have not yet been successful due to the fact that of the difficulty in designing membranes that will have better ionic conductivity than perfluoro sulphonic acid based membranes. These membranes have high ionic conductivity due to the due to the highly electronegative environment offered by fluorine atoms present in the polymer structure. Membranes with ionic conductivities comparable to that of perfluoro sulphonic acid polymers may be designed membranes which may possess ionic conductivity near comparable to that of Nafion® (Andolfatto et al 1994). This prospect is discussed in more detail as follows:

Nafion® a perfluorosulphonic acid based polymer, has high conductivity due to its extraordinary structural property. It consists of three regions:

- A fluorinated backbone (Polytetrafluoroethylene (or) Teflon-like backbone).
- Ion clusters consisting of \(-\text{SO}_3\text{H}^+\) ions. This \(-\text{SO}_3^-\) is fixed ion, while the \(\text{H}^+\) is mobile ion.
- Side chains of -O-CF₂-CF-O-CF₂-CF₂- containing -SO₃H groups that are connected to the molecular backbone.

when the membrane becomes hydrated, the H⁺ ions become mobile by bonding to the water molecules and moving between successive sulfonic acid groups. In dry state, the ion conductivity decreases. The combination of the perfluorocarbon (Teflon) polymer backbone and the sulfonic acid group provides excellent electrochemical and mechanical properties. High electronegativity due to fluorine atoms in the structure makes the polymer highly conductive.

2.14 PROTON CONDUCTING MEMBRANES

The migration of proton in water occurs by two different processes. The first is free solution diffusion process as vehicle mechanism as shown in Figure 2.8, where the fully hydrated membrane contains water phase similar to bulk water. Since the proton and associated water of hydration diffuse through water phase (Vandezande et al 2008) ionic conductivity is observed. The second process is Grothuss hopping mechanism as shown in Figure 2.9, where the proton moves by a succession of steps involving reformation and breakage of hydrogen bonds (Schäfer et al 2005). It involves both hydrophilic and hydrophobic part; the hydrophilic part is hydrated and helps to promote phase separation (Toh et al 2007). The hydrophobic part furnishes good mechanical stability even in presence of water while the hydrated hydrophilic phase provides the high proton conductivity.

Choi et al 2005 reported the thermodynamics and proton transport in Nafton membranes using a thermodynamic model that was proposed to describe the sorption of water in Nafton based on the Flory-Huggins activity model and an appropriate osmotic pressure correction term for the chemical potential of water within the swollen membrane. The key variables for
sorption are equivalent weight of ionomer, acid strength of the ionic groups, modulus of polymer elasticity, and interaction between water and polymer. The water uptake per unit mass of dry Naﬁon increases with the increasing acid strength of the functional groups that decreases the Young’s modulus and the equivalent weight of the membrane. The model provides insights into the sorption and swelling behaviour of ion-exchange membranes, and thus, may be useful in evaluating and designing alternate proton-exchange membranes for energy applications.

![Figure 2.8 The schematic view of vehicle mechanism](image)

![Figure 2.9 The schematic view of Grotthus hoping mechanism](image)

The proton transport in water is generally a result of protonic defects. This defect can weakens the intermolecular interaction which causes large variations in bond length combined with rapid breaking and forming of bonds. The proton hoping from H$_3$O$^+$ to a neighbouring water molecule which successively ejects one of the protons. This proton tends to form hydrogen bonds with a neighbouring water molecule. As a result, a succession of proton
hoping steps leads effectively to proton transport through the water (Li & Liu 2003). Thus the proton transport through a hydrated ion exchange membrane occurs via both of the two processes mentioned above (Lee et al 2005).

In composite membranes, the proton transport is through a hybrid mechanism because the inorganic component can also show vehicular mechanism (Tripathi & Shahi 2011). Hence, conduction may not reach the desired level that one observes in Nafion® due to the difficulty in creating an extraordinary electronegative environment similar to the one present in Nafion®. Water in the ion exchange membranes can be understood as bound water and bulk water. The bonding interaction between the bound water molecule and the material is greater than hydrogen bonding in the free water. So the bulk like-water is presumed to be a part of the materials. The free solution diffusion is much slower in bound water. In the transport by the vehicle mechanism the protons do not migrate as H⁺ but as complexes (Lufrano et al 2008) by diffusion across the inbuilt concentration gradient.

2.15 HYDROXYL CONDUCTING MEMBRANES

Polymer electrolyte membranes that can conduct OH⁻ ions have attracted a lot of attention in the recent years (Yu & Scott 2004; Gu et al 2009; Tanaka et al 2011; Cao et al 2012). Thin hydroxyl ion conducting membrane which offers low resistance is required for the operation of the alkaline cells (Merle et al 2011). During the last 60 years, hydroxyl conducting membranes have evolved from laboratory tool to industrial product with significant technical and commercial impacts. Soon after the early days of the development of polymer membranes, several limitations were recognized. For example, Sata et al (1999) reported a copolymer synthesized from chloromethylstyrene and divinylbenzene that turned out to be a carcinogen. Similarly, the use of chloromethyl methyl ether a potent carcinogen has been restricted since 1970 (Mclean et al 2002). Asbestos
separators, made using naturally occurring mineral, failed due to mechanical stresses induced by the formation of gas pockets within the separator (Sudhir et al 2007). It was found that zirconium phosphate, zirconium oxide, tin oxide, bismuth oxide, and lead sulfate (Vandenborre et al 1978, 1980) is chemically unstable in alkaline medium. Polybenzimidazoles (PBI) a complex polymer containing imidazole groups, that are not readily attacked by oxidizing agents, having high melting points and excellent stabilities at elevated temperatures (Glipa et al 1997); however, they do not withstand electrolysis conditions in alkaline medium.

Diaphragms of porous sintered material developed for alkaline water electrolysis have the disadvantage exists due to its of electron conducting property and high manufacturing cost (Divisek & Mergel 1983). Porous sheets of Teflon that have been made hydrophilic through in situ impregnation with potassium titanate fibers (Tomantschger & Kordesch 1989) could not be formed into matrices without a binder. The latter matrices proved to be stable over 2300 hours at 120°C. Nafion® membranes of two different equivalent weights were evaluated as a separator in an alkaline electrolyzer with nickel screen electrodes in both KOH and NaOH electrolytes over the concentration range of 10-30 wt%, showed maximum ionic conductance only under certain restricted conditions (Yeo et al 1980). Stojic et al (2008) compared alkaline and PEM electrolyzer and concluded that the alkaline electrolyzer had higher Faraday efficiency than the PEM electrolyzer, while less energy was required for the PEM electrolyzer compared to the alkaline one.

Varcoe & Slade (2005, 2006) prepared the hydroxyl conducting membrane that did not contain any metal cation (K⁺, Na⁺) ions to avoid the carbonate precipitation problem and to improve the long-term operation stability. Quaternary ammonium groups were bound to the polymer backbone
by radiation grafting onto ETFE, PVDF and FEP with hydroxyl ions as the counter ions for use as (Varcoe et al 2006) alkaline anion exchange membrane (AAEM).

Electro dialysis membranes that can transport anions are currently being studied for use in alkaline electrolysis cells. Hydroxyl ion conducting membranes based on Poly (ether ether ketone), polysulphone, and polystyrene are also currently being researched (Xiao et al 2012). Research and development of alkaline ion exchange membranes are focused on the improvement of transport properties for hydroxyl ions by increasing the density of fixed cationic groups, increasing the stability of the cationic group to nucleophilic substitution reactions, introduction of fluorine containing groups to improve stability (Leng et al 2012). Some of the membranes prepared consisted of two layers: a thin barrier layer of high equivalent weight polymer for the attraction of the counter ions (OH⁻) and a thicker layer of low equivalent weight polymer for strength.

Recently, Cao et al (2012) have prepared a quaternary ammonium grafted polyvinyl benzyl chloride membrane for use in alkaline anion exchange membrane water electrolyzers with Cu₀.₇Co₂.₃O₄ and nano Ni powder as oxygen and hydrogen evolution catalyst respectively. A current density of 100mA/cm² was obtained at 1.99V and 55°C. It has been reported that some hydroxide containing polymers shows promising performance in water electrolysis cells when in contact with aqueous alkali. The use of alkaline solution can increase the corrosion problems in the cell and auxiliary equipment. Improvement in membrane conductivity is due to the interface improvements between the membrane and the electrode assemblies (Gu et al 2009).

Wu and Scott (2012) developed the quaternary OH⁻ conductive ionomer binder for alkaline anion exchange membrane water electrolysis. The
conductivity of this ionomer attained 0.059 S/cm at 50°C. Further Xiao and co-workers (2012) implemented electrolysis by using alkaline polymer electrolyte made up of cross-linked quaternary ammonium Polysulfone membrane, which works on pure water, rather than KOH solutions. Recently Leng et al (2012) reported high performance anion exchange membranes (AEM) with a catalyst layer ionomer for OH⁻ ion conduction. They found that the durability of AEM based electrolysis cell could be improved by catalyst layer.

2.16 FACTORS AFFECTING PERFORMANCE OF MEMBRANES

There are number of factors that affect the performance of membranes. They are water uptake, swelling %, ion exchange capacity and thickness.

2.16.1 Water Uptake

Water uptake ($W_{wd}$) is defined as the ratio of the weight of water absorbed to that of the weight of the unabsorbed material. Water absorbed is measured after an equilibrium weight gain in the sample immersed in water.

$$W_{wd} (%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$  \hspace{1cm} (2.33)

where, $W_{dry}$ and $W_{wet}$ are the mass of the dry and wet membrane.

The proton conductivity of the membrane is dependent on the extent of water uptake (Andolfatto et al 1994). The proton conductivity generally increases with increase in water uptake. As the water molecule is absorbed in the membrane, there is an increase in the hydrophilic domain size resulting in the membrane swelling. As more water is absorbed in the
membrane, the cluster size increases and these clusters are connected to form water channels. This phenomenon is called percolation (Stauffer & Aharony 1992). These water channels provide the passage of protons. In essentially all the polymeric membranes, water is needed as the mobile phase to facilitate proton conductivity (Zhu et al 2006).

2.16.2 Swelling (%)

The membrane swelling characteristics were determined by measuring the change of the membrane geometrical area upon equilibrating the membranes in water at room temperature for 24h. The swelling ratio was calculated by the following Equation:

\[
\text{Swelling (\%)} = \frac{S_{\text{wet}} - S_{\text{dry}}}{S_{\text{dry}}} \times 100
\]

(2.34)

where, \(S_{\text{dry}}\) and \(S_{\text{wet}}\) are the area of dry and wet samples, respectively.

The electro-osmotic drag coefficient, is a quantitative measure of hydration, and can be defined as the number of water molecules transported per proton.

This parameter essentially defines the strength of the material. Water in the polymeric membrane acts as a plasticizer and decreases the strength of the membrane. Excessive water leads to membrane with low mechanical strength. In order to reduce the excessive swelling of ion exchanged membranes and enhance their lifetime reducing degradation processes, two primary strategies have been followed:

- Formation of cross-links with controlled swelling properties.
- Development of new materials more stable with regard to the physico-chemical processes in the electrolyser cell.
2.16.3 Degree of Sulphonation

The degree of sulphonation (DS) represents the number of sulphonic acids groups present in the ion exchange material. The conductivity in the polymer is dependent on the number of $\text{H}^+$ ions in the polymer which in turn depends on the number of sulphonic acid groups. In general as the degree of sulphonation increases in the polymer the conductivity increases. However, a polymer with high DS also leads to low strength material. Hence DS has to be at the optimum level. It is obtained by NMR or titration methods.

2.16.4 Ion Exchange Capacity

Ion exchange capacity (IEC) is the measure number of exchangeable ions in the polymeric material. The IEC of the membranes was determined using the following procedure. The dry composite membrane was immersed in 100 mL of 0.1M hydro chloride aqueous solution for 48 h to change them into $\text{H}^+$ form. The samples were then washed with distilled water to remove excess HCl, and then titrated with a standardized sodium hydroxide solution using phenolphthalein as an indicator. The IEC was calculated using the following equation.

\[
\text{IEC} = \frac{V \times M}{W_{\text{dry}}} \tag{2.35}
\]

where, IEC is the ion exchange capacity (mmol/g), V the added titrant volume at the equivalent point (mL), M the molar concentration of the titrant and $W_{\text{dry}}$ is the dry mass of the membrane (g).

2.16.5 Thickness

Thickness of the ion exchange material contributes to the resistance of the material to the passage of ions. Reduced thickness favors the membrane conductivity.
Advantages of reduced thickness include lower membrane resistance and hence an increase in membrane conductivity, lesser amount of the ion exchanges material (lower cost).

However, there is a limit to the extent to which membrane thickness can be reduced as mechanical strength and durability decreases (Noto et al 2012; Jung et al 2011). To obtain a balance between membrane thickness and membrane resistance, spatial control of charged regions can be carried out by surface modification and also by increasing the charge density in the microstructure of the PEM (Sudoh et al 2004) to obtain highly conductive materials.

2.17 POLYMER ELECTROLYTE MEMBRANE ELECTROLYSIS

Polymer electrolyte membrane water electrolysis (PEME) is an alternative method for hydrogen production. This method is more environmentally friendly and compatible with the usage of renewable energy sources. Recently, most studies related to electrolysis emphasize on the development of new advanced solid polymer electrolyte (SPE) based water electrolyzer as an efficient method for large-scale renewable high purity hydrogen production with minimal environmental impact.

One promising technology in water splitting is PEME that have high efficiencies (upto 75%) with which with the addition of catalyses typically Pt as catalyst for hydrogen evolution reaction (HER) and IrO₂ for oxygen evolution reaction (OER) (Horkans & Shafer 1977; Kong et al 2013). The polymer electrolyte membrane that is responsible for the conduction of ions is a key factor for better electrolysis performance. The most common membrane used in PEME is Nafion®. Researchers have focussed on other ion exchange materials and composites due to its high cost and limited operation
temperature range. Some of the non-fluorinated polymers such as Sulphonated Poly (Ether Ether Ketone) (SPEEK) (Lee et al 2012), Poly (Benzimidazole) (PBI), Sulphonated Poly sulfone (PSF) Zhang et al 2005; Yang & Manthiram 2003, Poly (Ether Sulfone) (PES), poly(arylene ethers), polyimides, and polyphosphazene (Qi & Huang 1994) have also been studied for their application as PEM Among these polymers, SPEEK and SPSF have shown superior properties such as excellent mechanical, thermal and chemical stability as well as good processability. PEEK were shown to be very promising is a thermo stable engineering polymers with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (-O-) and carbonyl (-CO-) linkages. The PEEK can be functionalized by sulfonation and the degree of sulfonation (DS) can be controlled by reaction time and temperature. The main problem with PEEK, however, is the high DS that is required to achieve sufficient proton conductivity; this causes PEEK polymers to become excessively water-swollen or water-soluble, thereby destroying their mechanical properties with a deleterious effect on the cell performance. For all these reasons, great interest has been focused on the development of alternative membranes for Nafion®. Organic-inorganic composite membranes for application in electrolyser performance has attracted attention, because such composites show controllable physical properties, such as ionic, thermal, and mechanical behaviour, by combining the properties of both organic polymers and inorganic compounds(Binsu et al 2005; Honma et al 2003).

SPE based water electrolyzer as an efficient method for large-scale renewable high purity hydrogen production with minimal environmental impact. A variety of organic polymers can be prepared based on the variation in the backbone structure, the degree of sulphonation, substituents, cross links etc. Low coat polymers with excellent chemical, mechanical and thermo oxidative stability and are low cost. Since they possess higher mechanical
stability sustainable over wide range of DS (Lassegues et al 2001) the mechanical stability of the polymer may be tuned based on the time and temperature of the reaction in order to achieve the desired DS, a factor that effectively controls the water splitting efficiency. It has been reported that a life time of more than 3000 h is important for their application as a proton conducting membrane material (Li et al 2005). More importantly, the DS has a strong influence on both conductivity and stability of SPEEK so we have selected SPEEK as aromatic material for fabrication of membranes.

More recently, Siracusano et al (2013) discussed the electrochemical characterization of a PEM water electrolyzer based on a sulfonated polysulfone membrane. In which the PEM based on a non-perfluorinated polymer PEM has been proposed as an alternative to Nafion for application in a water electrolyzer. The sulfonated polysulfone (SPSF) was synthesized using tri-methyl silyl chlorosulfonate as the sulfonating agent. The SPSF polymer was used for the preparation of a proton conducting membrane. A single cell PEM electrolyzer based on SPSF membrane, IrO$_2$ anode and Pt/C cathode electro catalysts was investigated by polarization, impedance spectroscopy, chrono-amperometry and gas crossover measurements. The performance was compared to that of an electrolyzer based on a standard Nafion$^\text{®}$115 membrane. The electrolyzer based on SPSF showed polarization and hydrogen permeation characteristics similar to those of Nafion$^\text{®}$ Membranes. After 35h potentiostatic operation at1.8V, the sulfonated polysulfone MEA reached a current density of 1.35A/cm$^2$. The results indicate promising performance of the sulfonated polysulfone polymer electrolyte membrane for application in a PEM electrolyzer.

In PEM based on SPEEK, SPSF etc. the sulphonic acid groups are attached to the backbone structure unlike per fluoro sulphonated polymers where the ionic groups are present in the side chains. As a result these
polymers lack a strong hydrophobic- hydrophilic group separation. The absence of strong electron with drawing groups in the backbone makes the polymers a weak acid compared to per fluoro sulphonated polymers (Kreuer (1996, 2001)). Ion clusters formed in these polymers is also small. Thus, even though the PEM based on these polymers are low cost; they are less efficient compared to the PEM based on per fluoro sulphonated polymers.

The concepts of PEM membranes normally have phase separate into hydrophobic polymer-rich phase domains and hydrophilic ionic cluster domains during the membrane formation process. When subjected to water, these ionic clusters absorb water to form a percolating network of ionic cluster containing water. The absorption of water takes place in two ways. (1) It occurs by solvation of the ions in the membrane (2) the percolating network of ionic clusters is formed during membrane swelling.

In general, proton conducting membranes are usually based on polymer electrolytes, which have negatively charged groups attached to the polymer backbone. These polymer electrolytes tend to be rather rigid and are fair proton conductors unless water is absorbed. The proton conductivity of hydrated PEM dramatically increases with increase in water content. In the case of perfluorinated polymer electrolytes, the structure of the electrolyte membrane in versatile states of hydration, the water uptake characteristics when exposed to water, and the properties of water in the PEM have all been investigated in detail (Krevelen & Nijenhuis 2009). The extreme hydrophobicity of the perfluorinated polymer backbone and the extreme hydrophilicity of the terminal sulfonic acid groups lead to a spontaneous hydrophilic-hydrophobic interaction. Thus the lower percentage of water uptake is due to the solvation of the proton and sulfonate ions. The higher percentage of water uptake corresponds to water involved in polymer swelling. In the former case, the water in the polymer is engaged in strong
interactions with ionic components of the polymer, and these interactions overcome the strong tendency of polymers to exclude water due to its hydrophobicity and resistance to swelling (Mulder 1996). Thus the SPE based electrolyzer technologies endure from the high cost of the catalysts and membranes, whereas non-SPE based electrolyzer technologies have the problem of low efficiency, corrosive nature and disposal of alkaline electrolytes that could cause environmental hazards (Kobayash et al 1998). Furthermore, the cost involved in the maintenance and handling of such technologies is considered to be higher than the SPE-based electrolyzer technologies.

2.18 METHODS TO IMPROVE THE PEM ELECTROLYSERS PERFORMANCE

There are various methods to improve the performance of the electrolyzers, they are:

- Increase reaction area (by adding inactive elements)
- Increase catalytic activity (by adding catalytic active elements)
- Increase reaction selectivity
- Increase stability

In general, at high current densities, the relationship between the trends in overpotentials is complex. This is due to the influence of mass transport and ionic resistivity on the high current overpotential. Hence using the differences between high and low current densities can yield information regarding the importance of structural aspects of the catalyst particles (Zecevic et al 1997). In order to achieve high efficiency and good catalytic performance, choice of parameters such as active surface area, specific
activity, electronic conductivity and particle structure are all important properties which are all need to be optimised.

2.19 ZERO GAP ELECTROLYSIS CELLS

For water electrolysis to become a more efficient system the energy loss has to be minimized and the overall cost has to be lowered. There are many attempts to make the electrolytical production of hydrogen more efficient. It is achieved by one among them is zero-gap electrolysis cell. Recent years have witnessed the evolution of zero gap electrolysis cells (Li & Pletcher 2011). The cells are constructed using the current collector that allow easy release of gas bubbles from the backside of the electrodes so as to minimize the ohmic voltage drop between the electrodes and electrolyte. Such a configuration is made due to the advancements in the AEM that are able to conduct hydroxyl ions. Zero gap cells have been developed with selected coatings on nickel such as Pt/ NiMo/RuO$_2$ etc. to improve the performance of the electrodes in AWE (Millet et al 1993; Pletcher et al 2012). The schematic view of zero gap cells is shown in Figure. 2.10.

Recently Li et al (2003) carried out stability tests in a zero gap cell with an OH$^-$ conducting membrane with a number of nickel based materials as potential oxygen evolution catalysts under high current density electrolysis conditions in alkaline water electrolysers. Microelectrodes were used to avoid distortion of voltammetric data by IR drop. High surface area nickel metal oxides prepared by cathodic deposition and mixed oxides prepared by thermal methods were used. A mixed Ni/Fe oxide was the preferred electro catalyst. The influence of hydroxide ion concentration and temperature on voltammetry was also investigated. The stability tests showed no significant increase in overpotential during 10 days operation in 4M NaOH electrolyte at a current density of 1 A/cm$^2$ at 60$^\circ$C.
It was found that applying a small voltage could not set off an electrolysis current, because the applied voltage must be at least as large as the theoretical cell voltage in order for a current to flow and to the release of hydrogen at the cathode and oxygen at the anode.

As the voltage was increased, the electrode surface absorbed more gas until a certain saturation point was reached where the gas pressure at the electrodes reached the level of external air pressure and gas bubbles begin to rise at the electrodes. A photographic view of zero gap cells is shown in Figure. 2.11. PEM technology operates in ‘zero-gap configuration where the electrodes are in direct contact with the surface of the separator membrane. The gap between the electrodes is the thickness of the membrane and distance that the ions have to travel in the electrolyte.
A smaller gap has the advantage of less resistance for ionic transportation. The electrolyte flow determines the mass transport in the electrolyte. To enhance mass transfer, the electrolyte was circulated. This cell concept offers some significant advantages compared to traditional electrolyzers systems and offers as follows:

- Reduced energy loss
- Possibility to operate at high current density,
- Low voltage losses in electrolyte,
- Low energy consumption (~ 4.0 kW/Nm$^3$ H$_2$),
- High specific productivity up to 2 A/cm$^2$,
- High hydrogen purity (>99.99%) and
- Possibility to operate at high pressures (30-50 bars).
2.20 GRAPHENE

Graphene a two-dimensional sheet composed of sp\(^2\) bonded carbon atoms with one-atom-thick carbon having high surface area, superior conductivity with high chemical and thermal stability (Geim & Novoselov 2007). It can be rolled into zero-dimensional spherical bucky balls, one-dimensional Carbon nano tubes and may be stacked into three-dimensional graphite. Treatment of graphite with strong oxidizing agents produces oxides which contain several functional groups such as carboxy, hydroxyl, carbonyl etc. on the surface. Graphene/ graphene oxide with transition metal/ metal oxide composites are also known to improve electrochemical activities (Kong et al 2013). It has been shown that graphene sheets can give rise to an extraordinary modification of the electro catalytic properties of Pt cluster on their surface (Yoo et al 2009). Such composite has been developed and used for application in Li ion batteries, super capacitors, electro chromic windows etc. The improved activity may be due to the stabilization of active form of the catalyst by bond formation between the metal ions and carboxyl groups of the graphene oxide through electrostatic attraction. Li et al (2008) prepared MOS\(_2\) nanoparticles on reduced graphene oxide sheets by solvo thermal synthesis for studying the electro catalytic activity in HER. The improved properties were attributed to the increase in catalytic edge sites and excellent electrical coupling to the graphene network (Vinayan et al 2013). Graphene is thus ideally suited for improving the electrochemical properties due to its high surface area, excellent conductivity, charge carrier sites, low production cost and scalability. It has been suggested that the carbon materials with a higher graphite percentage could be more stable (Jurcakova et al 2008) in electrochemical environments.

A specific branch of graphene research also deals with graphene oxide (GO). This can be analysed as a precursor for graphene. The common
preparation methods of graphene are: chemical exfoliation of graphite, chemical, electrochemical, thermal, and photocatalytic reduction of GO. The reduction of GO into graphene results in a graphitic structure that has single layer-graphene. The interlayer distance between the GO sheets increases between 6 Å and 10 Å with increasing relative humidity. It contains a large number of defects such as nanoholes and stone-wales defects (Gao et al 2013a). It is hard to make single layer-graphene of fine quality because of defect creation during exfoliation as a result of van-der Waals interactions between neighbouring sheets in graphene.

The theoretical specific surface area of graphene is reported to be 2630 m²/g, while that of graphite and SWCNTs are 15 and 1315 m²/g respectively (Lu et al 2010). The surface area in graphene is proportional to the porosity and it increases as porosity increased. The volumetric conductivity is decreased as the conductive pathways increases with increase in porosity. Graphene possess good electrical conductivity was caused by which include massless Dirac fermion, ambipolar electric field effect and extremely high carrier mobility and it can act as a zero-gap conductor (Kuila et al 2012). The vast array of current synthesis methodologies used for graphene manufacture includes:

- Exfoliation
- Chemical vapour deposition (CVD),
- Unzipping of CNTs
- Electrochemical method,
- Chemical methods,
- Physical methods.
2.20.1 Graphite Oxidation

Graphite oxide is mainly produced from the natural graphite flakes by the Brodie (1859), Staudenmaier (1898), Hummers & Offeman (1958) and modified Hummer’s method (Park & Ruoff 2009). Graphite oxide (GO) is a hydrophilic derivative of graphene. It consists of graphene sheets decorated mostly with hydroxyl and epoxide group. Due to its chemical structure, it works as an electrically insulating material. The properties of graphite oxide depend on the method of synthesis and the level of oxidation. All the method of synthesis involves oxidation of graphite in the presence of strong acids (H₂SO₄) and oxidants (KMnO₄). The level of oxidation can be varied depending on the reaction conditions and the graphite used.

2.20.2 Graphene Oxide

Graphene oxide shows great interest due to its low cost, scalability and widespread ability to convert to Graphene sheets. At present, the modified Hummers method is the primary method for preparing GO. The resulting brown substance of GO was prepared by chemical method and shown as Figure 2.12
2.20.3 Reduction of Graphene oxide: Chemical Method

Various procedures have been reported to obtain dispersible graphene (Gao et al 2009; Szabo et al 2005), i.e the exfoliated graphite by chemical, electrochemical, thermal reduction and chemical vapour deposition. Hydrazine is generally used to reduce a colloidal suspension of graphite oxide in distilled water to graphene. In a typical chemical procedure, graphene oxide was then added with distilled water to form yellow-brown dispersion.

![Figure 2.13 The photographic view of Reduced Graphene Oxide](image)

This dispersion was sonicated for 30 minutes to prepare the colloidal solution. Hydrazine hydrate was then added and the solution heated in an oil bath at 100°C for 24h over which the reduced graphene oxide gradually precipitated out as a black colour. The resultant black product was then filtered, washed with distilled water and dried it is shown in Figure 2.13. Shao et al (2010) reported that reduced graphene oxide shows much higher electrochemical capacitance and cycling durability than carbon nanotubes.
2.21 CARBON NANOTUBES

Nanotubes are one of the members of the fullerene family. Due to their superior physical and chemical properties, carbon nanotubes (CNTs) are recognized to have a vast potential in many fields of applications. In general, CNTs give special improvement to electrode performance due to their conducting networks and mesoporous structure. They also serve as excellent support material for metal oxides and conducting polymers giving attractive capacitor electrode materials. CNTs allow for the nanoscopic distribution of catalytic particles on the outer nanotubular surface for cathodic and anodic operations. The general preparation procedures include catalytic pyrolysis of hydrocarbons, arc and laser plasma techniques and low pressure condensation of carbon vapours.

Composite materials based on CNTs and inorganic nanomaterials are used in different energy devices (Liu et al 2012; Brownson & Banks 2010). The nanotubes align themselves into "ropes" held together by strong van-der Waals forces. CNTs can be categorized by their structures as single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) and double walled nanotubes (DWCNTs). SWCNTs can be considered as a seamless cylinder made by rolling a graphene sheet and MWCNTs can be composed of a series of concentric SWCNTs with an inter-tubes distance of ~0.32 nm. CNTs thus form a conducting route to improve charge propagation. As a group, CNTs typically have diameters ranging from 1 to 60 nm. Their lengths are typically few microns, but recent advancements have made the nanotubes much longer (Ouyang et al 2002). The strange electronic properties of 1 Dimensional CNTs are considered to arise mostly from the intra-layer interactions rather than from the inter-layer interactions of single CNT (Dai 2002). Since the CNT have become one of the active fields
of nanoscience and technology due to their peculiar properties that cause them adaptable for many potential applications.

2.21.1 SWCNTs

SWCNTs are made of a perfect graphene sheet of sp² carbon atoms rolled into a cylinder and closed by two caps. The internal diameter of these CNTs structures can vary from 0.5 to 2.5 nm (Ebbesen 1997) and the length ranges from few microns to millimeters. Many studied have demonstrated that they behave like one dimensional system where the electrons are held along the tube axis (Saito et al 1998; Hamada et al 1992). They can be considered as molecular wires with each atom on the surface. The fundamental SWCNT have a single walled structure with three different geometries namely armchair, chiral and zigzag.

2.21.2 MWCNTs

It consists of multiple rolled layers of graphite and exhibits various chiral structures. The electronic properties of MWCNTs may vary from semiconductors to metals, depends on the chiral angle. Due to the statistical probability and the limitations on the diameters of the individual tubes MWNTs is usually a zero gap metal where the number of walls varies from two to several tens. The inner diameters can be in the range from 1 nm to a few nm and the external diameter can be as short as hundreds of nanometer (Chiang & Ciou 2011; Treacy et al 1996). The external diameter depends on the number of layers.

2.21.3 DWCNTs

The morphology and properties of DWCNTs are similar to SWNTs. Since the resistance is based functionalization of the CNT,
DWCNTS have improved resistance. In the case of DWCNTs only the outer wall is modified (Javey & Dai 2005). The DWCNTs have an inner diameter of 2 nm and length of 30 μm in size.

2.22 GRAPHENE- NICKEL COMPOSITES

On the purpose to improve their further performance, some researchers used metal foam instead of metal mesh to strengthen the corrosion resistance and decrease the weight so as to improve their performance (He et al 2006). Moreover electrical conductivity was higher for the MEA made of Ni foam rather than that made of traditional one to increase the cell performance. Nickel foam has a lower weight/surface ratio and is accordingly less expensive than nickel mesh. Thus the nickel foam is very attractive due to its high porosity, high specific surface area, corrosion resistance, low density, high mechanical strength and good electrical conductivity. Deposition techniques including electro-deposition (Dai et al 2008), electroless deposition, and impregnation-reduction methods followed by thermal treatment (Chen et al 2007) have all been established with nickel foam.

Many studies have been carried to explore for advanced materials to support the electro catalysts for OER, such as formation of metal oxide, chemical modification and versatile forms of carbon materials. Among them, carbon materials, including carbon nanofibers, carbon nanotubes and porous carbons are the typical support materials for MEAs, a recent addition of which is the single atomic layer graphite, graphene oxide.

Literature studies have thus shown that Ni based electrodes are suitable for alkaline water electrolyzers. Further studies on graphene have shown that enhancement in electrochemical properties can be achieved by the use of graphene/graphene oxide in the electrodes. Since the development a zero gap alkaline anion exchange membrane based electrolyzer which
incorporates Ni based catalysts that have been modified with graphene oxide and study its properties is a major research area. The effect of the modified electrode on performance in alkaline water electrolyzer was optimized in terms of temperature, concentration of the alkali solution and stability.

Since Nickel based alloys have constituted high electro catalytic activity in OER and exhibited the better electro catalytic capability than an individual Nickel catalyst for synergistic electronic effect among the alloys. Furthermore graphene is ideally suited for accomplishing in electrochemical applications due to its reported large electrochemical performance, vast surface area and charge carrier sites, As a result, GO is an awesome host matrix for the interlayer adaptation of hydrocarbons and transition metal ions and is also promising for particle engineering processes, especially for the fabrication of electrode materials with smart properties. Therefore an aggregation of a large surface area with an enhanced electro catalytic activity and charge carrier sites enable deposits GO on nickel foams (Cai et al 2012). Thus the 3- dimensional current collectors considerably reduce the internal resistance of the electrode by improving the electronic contact between the graphene and the collector.

2.23 POLYMER-CARBON COMPOSITES

To improve the electrolysis efficiency of polymer membranes, polymer composites were prepared with filler particles that raise the conductive state and improve the charge transport through the polymer matrix (Pandey et al 2010; Shimizu et al 2008). Polymer carbon composites were prepared with CNT and reduced graphene Oxides (RGO) as filler to enhance the conductivity. The unique properties of these types of composites provide novel electrical, magnetic, mechanical, thermal, and other features that are desirable for applications in commercial, medical, military, and environmental sectors (Perera et al 2012). Moreover the direct mixing of
carbon materials with polymer followed by sonication is straightforward process.

Tseng et al 2011 reported that the sulfonated polyimide-graphene oxide composite membranes show improved proton conductivity and mechanical properties. Composite membranes with 0.5% graphene oxide showed higher proton conductivities than Nafion® 117 and a maximum conductivity were achieved at 90ºC. Graphene oxide in the membrane not only promoted high proton conductivity, it also had a positive effect on the mechanical properties and the permeability of methanol molecules across the membrane (Marcano et al 2010). Further the membranes promote internal self-humidification effects that increase their conductivity and ease water management even at high temperatures and under low humidity conditions. MWCNTs have some defect density. This is due to the statistical probability and their limitations on the diameters of the individual tubes that could dramatically change the surface properties and increase the conductivity (Yu et al 2011). It has high conductivity, large surface area, wide electrochemical potential window and good chemical stability which make them ideal as materials for composite fabrication (Gao et al 2013b). Since the CNTs have attracted a tremendous amount of concern because of their unique shape. The rolled structure of the graphite sheets has gathered much attention from both theoretical and practical aspects in physics and chemistry (Dresselhaus et al 2010).

The CNT/ polymer composites are being explored by many researchers for improved electrochemical properties. Similarly graphene based composites have also shown outstanding conductivity and tensile strength (Zhao et al 2010). The oxygenated groups in graphene oxide are highly dispersible in aqueous solutions. Hence it can be easily processed into films, rolls and nanocomposite membranes (Lv et al 2010).
Reduced graphene oxide has the characteristics of large area, outstanding conductivity and tensile strength. Graphene oxide does not show good conductivity due to the presence of oxygenated functional groups and adsorbed water molecules on either sides of the basal plane (Ling et al 2013). Composites membranes based on graphene oxide and sulphonated polymers have enhanced mechanical properties, large surface areas, high porosity, good chemical stability, rigidity, and most importantly outstanding conductivity, leading to higher efficiency. So far the application of CNT/GO supported nanocomposite membranes has been limited to fuel cells applications only (Kauffman et al 2010; Su et al 2010).

A study to compare and explore the possibility of using the sulphonated polymer/RGO and sulphonated polymer/CNT nanocomposite membranes as a platform for the development of water electrolysis application was undertaken. Due to the presence of these productive functional groups, RGO nanosheets are highly dispersible in aqueous solutions, and can be easily processed into films, rolls and composites. (Sang et al 2011) Moreover, the effective properties of the composites are dependent upon the properties of components, size, shape and arrangement of inclusions and interfacial interaction between polymer and the matrix (Yasmin et al 2006).

2.23.1 Preparation Methods of Polymer- Carbon Composites

The direct mixing of carbon materials i.e (Graphene/CNT) with polymer is a straightforward process, which involves:

- Suspensions of carbon in polymer solutions,
- In-situ polymerization in presence of nanotubes
- Melt mixing of carbon with polymers
However, agglomeration of carbon should be avoided while formation of the composite. Non agglomerated composite is required for network formation of the filler and for uniform mechanical properties (Fang et al 2009).

2.24 POLYMER -HETEROPOLYACIDS COMPOSITES

In order to address the one of the methods to overcome the limitations of sulfonated ionomers is to prepare composite membranes. Organic-inorganic proton-conducting membranes contain various inorganic components added to the polymer host. Among the various inorganic components as Heteropolyacid (HPA) incorporated with TiO\textsubscript{2} for catalytic applications. (Chen et al 2007) has been the focus of many research articles. The choice of these fillers is based on the assumption that the filler properties could possibly provide extra mobile protons as charge carriers and serve as ‘proton conducting materials’ (Noto et al 2010; Li et al 2003) or because of their ability to retain water to overcome the limitations of perfluorosulphonic acid membranes.

HPA (Helen et al 2007) in addition have a dual role of hydrophilicity and proton conducting materials. However, HPAs are generally water-soluble. Their degree of solubility is reduced in composite HPAs without a compromise of their proton conductivity (Zhang & Zhou 2005). Consequently, a large number research objective is to fix the HPAs in stable form by forming composites, which can preserve their high proton conductivity. HPAs are generally composed of i) a metal such as tungsten, molybdenum or vanadium, ii) oxygen, iii) some of the element from the p-block such as phosphorous, silicon or arsenic and iv) acidic hydrogen atoms. The conjugate anions of the HPAs are known as poly-oxo metalates, having M-O (metal-oxygen) octahedral as the basic structural unit. The Keggin type anion is composed of a central tetrahedron XO\textsubscript{4} surrounded by 12 edge and
corner sharing M-O octahedral $\text{MO}_6$. In general HPAs form ionic crystals composed of heteropolyanions, counter cations like $\text{H}^+$, $\text{H}_3\text{O}^+$ and hydrated water molecule. This water molecule can be easily removed by heating, whereby the acid strength is increased owing to the dehydration of protons. Not only water but also a variety of polar molecules can enter and leave HPA crystals. This Keggin structure has some of the highest reported solid state proton conductivities. Their proton transport have been extensively reported (Adjemian et al 2002) and have become popular proton conducting additive in proton exchange composite membranes for use at elevated temperatures. They are pure bronsted acids as well as stronger acids than the conventional solid state acids such as $\text{SiO}_2$, $\text{H}_3\text{PO}_4$ and $\text{Al}_2\text{O}_3$. Hence the acid forms have low surface acidity due to less number of acidic sites on the surface, have low surface area and are highly soluble in water. Partial substitution of the proton by a large monovalent ion such as $\text{Cs}^+$ results in unique changes in the surface area and solubility making then insoluble in water.

Formation of composite matrix with large moiety cations like $\text{Cs}^+$, $\text{Rb}^+$ and $\text{NH}_4^+$ (Kreuer 1988; Ramani et al 2005) by ion exchange process reduces leaching of HPAs. Composite membrane prepared by incorporation of cesium salts of silicotungstic acid (CsSiWA) and inorganic fillers (Birnie et al 2006) such as titanium dioxide ($\text{TiO}_2$), silicon dioxide ($\text{SiO}_2$), zirconium dioxide ($\text{ZrO}_2$) into partially sulfonated polyether ether ketone (PEEK) polymer matrices have been reported. Hence HPAs have been incorporated into the membranes to improve their structure and conductivity and produce composite membranes. It increases the binding energy of water and proton conductivity. HPA-incorporated composite solid electrolyte membranes for energy applications have been given more attention in recent years (Ponce et al 2003).
Salts of HPAs may be prepared at room temperature by neutralization with cesium carbonate followed by drying process at room temperature. It can also be prepared by precipitation titration (Li et al 2006) method where to the aqueous solutions of HPA, cesium carbonate solution was added drop wise with stirring in room temperature. The precipitate was recovered from the colloidal solution by evaporation of liquid phase at 60ºC followed by heating to 350ºC. The powders of cesium salt of phospho tungstic acid and cesium salt of phospho molybdic acid were obtained by heating at 350ºC for 1h. Finally, prepared powders were grinded and dried in vacuum oven at 70ºC.

2.25 ORIGIN OF THE STUDIES FROM LITERATURE SURVEY

Literature studies have thus shown oxygen evolution reaction has high overpotential and leads to most of the losses in an electrolyzer system. Literature studies have also shown that Ni based electrodes may be used in AWE system. Electrodeposition is an important method of fabrication of alloy electrodes and it can be carried out in many ways. An optimised electrode with high performance is required for AWE system based on these findings it was proposed to develop Ni electrodes by direct electro deposition, pulse electrodeposition, sonoassisted direct electrodeposition and sonoassisted pulse electrodeposition technique. OER studies were also carried out in the presence of stabilizers/ complexing agents for further improvements in the performance. An alkaline anion exchange membrane based water electrolyzer cell was fabricated with the optimised electrode preparation technique. Ni foam was used as the substrate for the electrodes with aim to improve the contact between the membrane and the electrode as it has high surface to weight ratio. Nickel foam is an attractive substrate as it has high porosity, specific surface area, corrosion resistance, low density, high mechanical strength and good electrical conductivity (He et al 2006). Ni electrodes may
be prepared from Ni foam using deposition techniques like electro-deposition (Dai et al 2008), electroless deposition, and impregnation-reduction methods, by thermal treatment (Chen et al 2007) methods.

Literature studies also have shown that composite polymer membranes have better conductivity and mechanical properties (Srinivasan 2006). Hence, it was proposed to develop low cost polymer composites as alternative to conventionally used perfluorosulphonic acid membranes and study their performance in water electrolyzers. Towards this polymer- carbon composites and polymer- metal oxide- heteropolyacid composites were developed for water electrolysis applications.