ELECTROCHEMICAL ENERGY SYSTEMS

Electrochemical Cells

In an electrochemical cell, chemical energy can be converted into electrical energy and vice versa. There are two types of electrochemical cells – galvanic cells and electrolytic cells.

Galvanic Cells or Voltaic Cells

A galvanic cell or Voltaic cell is a device in which chemical energy is converted into electrical energy in a redox reaction.

A galvanic cell consists of 2 half cells, each containing an electrode dipped into a solution of the electrolyte of its own ions. The two half cells are connected externally by a conducting wire through a galvanometer and internally by a salt bridge. The electrode at which oxidation takes place is called anode and that at which reduction takes place is called cathode. A typical example for a galvanic cell is the Daniel Cell.

Daniel Cell

Daniel Cell consists of a Zn rod dipped in ZnSO₄ solution and Cu rod dipped in CuSO₄ solution taken in two separate vessels. The two metal rods acting as electrodes are connected externally by a conducting wire through a voltmeter. The two electrolytes are connected internally by a salt bridge. The salt bridge is filled with aqueous solution of some inert electrolytes such as KCl, KNO₃, or NH₄NO₃ to which gelatin has been added to convert it in to a semisolid paste.
The deflection in the voltmeter indicates that there is a potential difference between the 2 electrodes. Electron flow from Zn electrode to Cu electrode but current flows from Cu to Zn. The emf of the cell is 1.1 V which is due to the following cell reactions,

Anode reaction; \[ \text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^- \]

Cathode reaction; \[ \text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)} \]

Cell reaction; \[ \text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)} \]

Daniel Cell

The symbolic representation of a Daniel Cell is Zn/Zn\(^{2+}\)//Cu\(^{2+}\)/Cu
Electrode Potential

The tendency of a metal electrode to lose or gain is when it is in contact with its own salt solution is called electrode potential. If the tendency of an electrode is to lose electrons, then it is called oxidation potential and if the tendency is to gain electrons it is called reduction potential. For the same electrode, oxidation and reduction potential are numerically the same, but with opposite sign. For eg. Reduction potential of Zn electrode is \(-0.76\) v and its oxidation potential is \(+0.76\) v.

The electrode potential of an electrode under standard conditions i.e. the concentration of the solution is IM and temp is 298 k, it is called standard electrode potential.

Standard Hydrogen Electrode (SHE or NHE)

The standard hydrogen electrode is a gas ion electrode which is used as a reference electrode for measuring the electrode potential of other electrodes.

It consists of a Pt wire sealed in to a glass tube and has a Pt foil attached to it. The foil is coated with finely divided Platinum and acts as Pt electrode. It is dipped into IM HCl solution. The Pt foil is surrounded by an outer glass tube which has an inlet at the top to admit H\(_2\) gas and a number of holes at the base for the escape of excess H\(_2\) gas.
The cell may be represented as Pt, $\text{H}_2\text{(1 atm)}/\text{H}^+/(\text{IM})$. The following reactions occur in this half cell depending on whether it acts as anode or as cathode.

Acting as anode,

$$\text{H}_2(\text{g}) \rightarrow 2\text{H}^+ + 2e$$

Acting as cathode,

$$2\text{H}^+ + 2e \rightarrow \text{H}_2(\text{g})$$

The potential of this electrode is arbitrarily fixed as zero.

**Limitations**

1. the Pt surface must be specially prepared and maintained.
2. The gas pressure need be controlled.
3. The electrode cannot be used in the presence of strong oxidizing and reducing agents.
4. Expensive due to Pt metal.
5. It cannot be used in presence of ions of many metals.
6. Constant supply of $\text{H}_2$ gas.

**Applications**
1. Used as a reference electrode for measuring the electrode potential of other electrodes.

2. Used in the determination of $P^H$.

**NERNST EQUATION**

The relation between electrode potential and concentration of electrolyte solution is given by Nernst equation. For a general reaction of the type, $M^{n+} + ne \rightarrow M(s)$, the Nernst eqn is given by,

$$E = E^\circ + \frac{2.303 \cdot RT}{nF} \log (M^{n+})$$

Where, $E$ = Electrode potential at given concernn.

$E^\circ$ = Standard electrode potential.

$R$ = gas constant (8.314 J/K/mol)

$T$ = absolute temp

$N$ = number of es involved in electrode reaction

$F$ = Faraday’s constant

$((M^{n+}))$ = Concentration of electrolyte.

From the equation it is clear that,
1. Electrode potential increases with the increase in concentration of the electrolyte.

2. Electrode potential increases with the increase in temp.

**Derivation of Nernst Equation**

Consider a general reversible redox reaction of the type,

\[ M^{n+}(aq) + ne \rightleftharpoons M(s) \]

For a reversible reaction, the free energy change (\( \Delta G \)) and its equilibrium constant (Kc) are interrelated according to Van’t Hoff reaction isotherm,

\[ \Delta G = \Delta G^\circ + RT \ln Kc \]

Or

\[ \Delta G = \Delta G^\circ + RT \ln (\text{Product}) \]

\[ \quad \text{--------------- where} \]

\[ \Delta G^\circ \text{ is the standard free energy change} \]

For the above reversible reaction, the isotherm can be written as,

\[ \Delta G^\circ = \Delta G^\circ + RT \ln (M) \]

\[ \quad \text{(M}^{n+}) \]

In a reversible electrode reaction the electrical energy produced is equal to the decrease in free energy. The electrical energy produced in a cell is equal to the quantity of electricity x emf. i.e. Electrical energy = qty of electricity x emf

\[ = nF \times E = nFE \]

\[ \therefore \Delta G = nFE \]
or $\Delta G = -nFE$

and

$\Delta G^\circ = -nFE^\circ$ --- (2) where $E^\circ$ is the standard electrode potential.

Equating eqns (1) and (2)

$-nFE = -nFE^\circ + RT \ln \frac{M}{(M^{n+})}$

Dividing by $-nF$

$E = E^\circ - RT \ln \frac{M}{(M^{n+})} (nF)^{-1}$

Or $E = E^\circ - 2.303 RT \log \frac{M}{(M^{n+})} (nF)^{-1}$

Taking the concentration of metal as unity equation becomes.

$E = E^\circ - 2.303 RT \log \frac{1}{(M^{n+})} (nF)^{-1}$

or $E = E^\circ + 2.303 RT \log (M^{n+}) (nF)^{-1}$

This is Nernst equation.

When $T = 298$ K, $R = 8.314 \text{ J} \text{K}^{-1}\text{mol}^{-1}$ and $F = 96500 \text{ C}$, the equation becomes,
E = \text{E}^\circ + -2.303 \text{RT} \quad \frac{\log (\text{M}^{\text{n}+})}{\text{(nF)}}

Problems

1. In rod is placed in a a 0.1M solution of Zinc sulphate at 25°C. Calculate the potential of the electrode at this temp assuming 96% dissociation of ZnSO4 and \text{E}^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76V

Solution

Concentration of Zn^{2+} with 96% of dissociation

= 0.1 \times 96/100

= 96 \times 10^{-3}\text{M}

The electrode reaction is Zn^{2+}_{(aq)} + 2e \rightleftharpoons Zn(s). According to Nernst equation, the potential of the electrode is

\[
E = \text{E}^\circ + -2.303 \text{RT} \quad \frac{\log (\text{Zn}^{2+})}{\text{(nF)}}
\]

\[
= (-0.76) + -2.303 \times 8.314 \quad \frac{\log (96 \times 10^{-3})}{2 \times 96500}
\]

= -0.79 V

======

2. Find the single electrode potential of the electrode Cu/Cu^{2+}_{(0.2M)}; if \text{E}^\circ=0.34V (R = 8.314 J K^{-1}mol^{-1}, T = 298 K)

Solution
\[ E = E^\circ + \frac{-2.303 RT \log (\text{Cu}^{2+})}{(nF)} \]

\[ = 0.34 + \frac{-2.303 \times 8.314 \times 298 \log (0.2)}{2 \times 96500} \]

\[ = 0.34 + 0.0296 \log 0.2 \]

\[ = 0.34 + 0.0296 \times -0.6990 \]

\[ = 0.34 - 0.0207 \]

\[ = 0.3193 \text{ V} \]

**Applications**

1. Calculation of electrode potential

2. Calculation of emf

3. Calculation of conc. Of a solution of a half cell.

4. Determination of PH of a solution

5. Calculation of eqm const of a reaction

**EMF of a cell or Cell Potential**

Electromotive force or emf can be defined as the driving force that arises from a difference of potential which causes the current to flow from an electrode at a higher potential to an electrode at a lower potential. It is measured in volts.
The emf of a cell can be calculated from the values of the electrode potentials of the two half cells constituting the cell.

ie. \( E_{cell} = \text{Reduction Potential of Cathode} - \text{Red}^a \text{ potential of anode} \)

\[
E_{cell} = E_R - E_L
\]

and \( E^{\circ}_{cell} = E^{\circ}_R - E^{\circ}_L \)

If the value of EMF obtained is +ve then it indicates that the cell reaction is spontaneous and its negative value indicates that the cell reaction is non spontaneous

**Nernst Equation for EMF of a cell**

EMF of a cell can be calculated using Nernst equation.

Consider the cell, \( M_1(s) / M_1^{n^+} (aq) C_1 // M_2^{n^+} (aq) C_2/M_2(S) \)

The cell reaction is given by

\[
M_1(s) / M_2^{n^+} \rightarrow M_1^{n^+} + M_2(S)
\]

\[
E_{cell} = E^{\circ}_{cell} + \frac{-2.303 RT}{\log \frac{C_2}{C_1}} \quad \text{(reactant)}
\]

\[
E_{cell} = (E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{anode}}) + \frac{-2.303 RT}{\log \frac{C_2}{C_1}} \quad \text{(nF)}
\]

ie. \( E_{cell} = (E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{anode}}) + \frac{-0.0592 RT}{\log \frac{C_2}{C_1}} \quad \text{(nF)}\)

Where \( E_{cell} = \text{EMF of the cell} \)

\( E^{\circ}_{cell} = \text{Standard EMF of the cell} \)
E°_Cathode = Standard electrode potential of cathode
E°_anode = Standard electrode potential of anode
n = Number of ens involves in the reaction
C₁ = Concentration of electrolyte in the left hand half cell
C₂ = Concentration of electrolyte in the right hand half cell.

**Measurement of EMF by Poggendorf’s Compensation Method**

The emf of a cell cannot be measured directly by connecting it with a voltmeter because a part of the current is drawn by the voltmeter to overcome its internal resistance. Hence the measured emf is less than the actual emf. It is usually measured using a potentiometer which makes use of the compensation principle. In this method, the unknown emf is opposed by another known emf until the two are equal.

**Procedure**

Potentiometer consists of a uniform wire AB of high resistance. The two ends of this wire are connected to a storage battery C whose emf is constant and greater than that of either the given cell or the std. cell. The cell X whose emf (Ex) is to be determined is connected to the circuit through a galvanometer G and a sliding contact J. The 1st circuit is completed by introducing key K1.
The battery sends a current through the galvanometer in a direction opposite to that in which the current is sent by the cell with unknown emf. The sliding contact is moved along the wire AV till the point D is reached when no current flows in the circuit. The balancing length AD is measured.

\[ \text{i.e. } E_x \propto \text{length AD} \]

The experiment is repeated by replacing the cell X by the std. Cell S. Thus the 2\textsuperscript{nd} circuit is then completed through std. cell S of known emf (Es) by introducing key K2. The sliding contact is again moved along the wire AV till the point D’ is reached, when no deflection is observed in the galvanometer. The distance AD’ is also measured.

\[ \text{i.e. } E_x \propto \text{length AD’} \]

\[ \therefore \frac{E_x}{E_S} = \frac{\text{length AD}}{\text{length AD’}} \]

Or \[ E_x = \frac{AD \times E_S}{AD’} \]
Since $E_s$ is known, the unknown emf $E_x$ of the cell can be calculated.

**Problems**

1. Find the emf of the cell $M_g/M_1^{n+} (aq) // Cd^{2+} (aq)/Cd(s)$ at $25^\circ C$ if $(cd^{2+}) = 6 \times 10^{-11} M$ and $(mg^{2+}) = 1 M$

   Soln.

   $$Mg(s) + Cd^{2+} (aq) \rightarrow Mg^{2+} (aq) + Cd(s)$$

   C2 = $(cd^{2+}) = 6 \times 10^{-11} M$, C1 = $(Mg^{2+}) = 1 M$, $E^{\circ}_{cell} = 1.97 V$

   $$E_{cell} = E^{\circ}_{cell} + 0.0592 \log \frac{C2}{nC1}$$

   $$= 1.97 + 0.0592 \log \frac{Cd^{2+}}{Mg^{2+}}$$

   $$= 1.97 + 0.0592 \log \frac{6 \times 10^{-11}}{1}$$

   $$= 1.97 + 0.0296 \times 10.2218$$

   $$= 1.97 - 0.3026$$

   $$= 1.667 V$$

**Types of Electrodes**

When a metal rod is dipped in its salt solution, it acts as an electrode. Electrodes are the essential parts of an electrochemical cell. Electrical circuit in a cell is completed by means of electrodes. The chemical reactions in a cell occur at the electrodes. The
electrode where oxidation takes place is called the anode and the electrode where reduction takes place is called the cathode. There are different types of electrodes in common use.

i) Metal – Metal ion electrode

These types of electrodes consist of a metal rod dipped in the solution of its own ions. Examples are Zn rod dipped in ZnSO4 solution and Cu rod dipped in Cu SO4 solution.

\[ \text{Zn(s)/Zn}^{2+}_{(aq)}; \text{Zn(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e \]

\[ \text{Cu}^{2+}_{(aq)}/ \text{Cu(s)} ; \text{Ca}^{2+}_{(aq)} \rightarrow \text{Cu(s)} \]

ii) Metal – Metal insoluble salt – anion Electrode

This consists of a metal rod in contact with its sparingly soluble salt and a solution of a soluble salt containing the same anion. Eg: Calomel electrode

**CALOMEL ELECTRODE**

Calomel electrode is commonly used as a secondary reference electrode for potential measurements. It consists of Hg in contact with a solution of KCI saturated with Hg2Cl2.

Calomel electrode consists of a glass tube at the bottom of which is placed a small amount of mercury. Over this is placed a paste of Hg & Hg2Cl2. The remaining portion of the tube is filled with 0.1 N or IN or saturated KCI solution. A pt wire dipping in to the Hg layer is used for electrical contact. The glass tube is having side tube on each side. One side tube is used for making contact with a salt bridge and the other side tube is to introduce KCI solution. The electrode may be symbolically represented as : Hg, Hg2Cl2(s)/KCI(sat)
When combined to other electrodes, it can act as an anode or cathode depending on the nature of other electrode. When it acts as an anode the electrode reactions are:

\[2\text{Hg} + 2 \text{cT} \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e} \]

When it acts as a cathode the electrode reaction is,

\[\text{Hg}_2\text{Cl}_2 + 2\text{e} \rightarrow 2\text{Hg} + 2\text{cT} \]

Hence the electrode is reversible with respect to cT ions. The potential of this electrode depends up on the concentration of KCl used. Calolele electrode is used for measuring the potential of other electrodes.

iii) **Gas Electrode**
These electrode consists of a gas bubbled around an inert metal wire, usually pt immersed in a solution capable of furnishing the ion of the gas. The function of the metal wire is to establish an equilibrium between the gas & its ions and also to make electrical contact. H₂-electrode, Cl₂ electrode and O₂ electrode are common examples.

a) Hydrogen electrode

b) Cl₂ electrode

The electrode may be represented as Cl₂(g)/u/graphite. In this electrode Cl₂ gas at a given pressure is passed into hydrochloric acid which supplies cT ions. For oxidation to take place, the following reactions occur,

\[ 2cT \rightarrow Cl₂(g) + 2é \]

For reduction to take place, the following reaction occur,

\[ Cl₂(g) + 2é \rightarrow 2cT \]

Thus this electrode is reversible with respect to cT ions.

iv) **Oxidation – Reduction Electrodes**

An oxidation – reduction electrode has an inert metal collector, usually pt immersed in a solution containing two soluble salts of the same metal with different valancies. The potential is developed due to tendency of metal ion to pass from less stable oxidation state to more stable oxidation state. An eg: is the ferric – ferrous ion electrode. \( Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)}/pt. \)
v) **Glass Electrode**

A glass electrode is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. It is an important part of the instrumentation for chemical analysis and physico-chemical studies. In modern practice, widely used membranous ion-selective electrodes (ISE, including glasses) that are part of a galvanic cell. The electric potential of the electrode system in solution is sensitive to changes in the content of a certain type of ions, which is reflected in the dependence of the electromotive force (EMF) of galvanic element concentrations of these ions.

**Construction**

A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The combination electrode consists of the following parts (see the drawing):

1. a sensing part of electrode, a bulb made from a specific glass
2. sometimes the electrode contains a small amount of AgCl precipitate inside the glass electrode
3. internal solution, usually 0.1 mol/L HCl for pH electrodes or 0.1 mol/L MeCl for pMe electrodes
4. internal electrode, usually silver chloride electrode or calomel electrode
5. body of electrode, made from non-conductive glass or plastics.
6. reference electrode, usually the same type as 4
7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.

The bottom of a pH electrode balloons out into a round thin glass bulb. The pH electrode is best thought of as a tube within a tube. The inside most tube (the inner tube) contains an unchanging saturated KCl and a 0.1 mol/L HCl solution. Also inside the inner tube is the cathode terminus of the reference probe. The anodic terminus wraps itself around the
outside of the inner tube and ends with the same sort of reference probe as was on the inside of the inner tube. Both the inner tube and the outer tube contain a reference solution but only the outer tube has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge.

- The details of this section describe the functioning of two separate types of glass electrodes as one unit. It needs clarification.

This device is essentially a galvanic cell that can be represented as:

\[
\text{Ag} | \text{AgCl} | \text{KCl solution} \parallel \text{glass membrane} \parallel \text{test solution} \parallel \text{ceramic junction} \parallel \text{KCl solution} | \text{AgCl} | \text{Ag}
\]

The measuring part of the electrode, the glass bulb on the bottom, is coated both inside and out with a ~10 nm layer of a hydrated gel. These two layers are separated by a layer of dry glass. The silica glass structure (that is, the conformation of its atomic structure) is shaped in such a way that it allows Na\(^+\) ions some mobility. The metal cations (Na\(^+\)) in the hydrated gel diffuse out of the glass and into solution while H\(^+\) from solution can diffuse into the hydrated gel. It is the hydrated gel, which makes the pH electrode an ion selective electrode.

H\(^+\) does not cross through the glass membrane of the pH electrode, it is the Na\(^+\) which crosses and allows for a change in free energy. When an ion diffuses from a region of activity to another region of activity, there is a free energy change and this is what the pH meter actually measures. The hydrated gel membrane is connected by Na\(^+\) transport and thus the concentration of H\(^+\) on the outside of the membrane is 'relayed' to the inside of the membrane by Na\(^+\).

All glass pH electrodes have extremely high electric resistance from 50 to 500 M\(\Omega\). Therefore, the glass electrode can be used only with a high input-impedance measuring
device like a pH meter, or, more generically, a high input-impedance voltmeter which is called an electrometer.

CONCENTRATION CELLS

Concentration cells are those in which the emf is produced due to difference in concentration of either the electrode or the electrolyte. Thus a concentration cell contains two half cells made up of identical electrodes and identical electrolytes connected by a salt bridge and the difference observed will be either different electrode concentration or
different electrolyte concentrations. In a concentration cell there is no net chemical reaction. The transfer of substance from a solution at a higher concentration to one at lower concentration produces electrical energy.

Concentration cells are of 2 types:

i) Electrode concentration cell

ii) Electrolyte concentration cell

**Electrode concentration cell**

In an electrode concentration cell the electrodes themselves have different concentration. They may be gas electrodes operating at different pressures or amalgam electrodes with different concentrations.

Eg: Zn\(_{(Hg) C_1}\) → ZnSO\(_4\) + Zn\(_{(Hg) C_2}\)

**Electrolyte Concentration Cell**

An electrolyte concentration cell is made up of two half cells having identical electrodes immersed in two solutions of the same electrolyte at different concentrations. The electrical energy arises from the transfer of a substance from a solution of higher concentration to a solution of lower concentration.

A general electrolyte concentration cell may be represented as;

\[ M_{(s)} / M^{n+}_{(a)}/M^{n+}_{(C2)}/M_{(s)} \]

The cell reactions are

Anode \( M \rightarrow M^{n+}_{(C1)} + ne \)

Cathode \( M^{n+}_{(C2)} + ne \rightarrow M_{(s)} \)
The overall cell reaction is

\[ M^{n+}(C_2) \rightarrow M^{n+}(C_1) \]

The emf of the cell is given by Nernst equation as,

\[
E_{\text{cell}} = \text{ER} - \text{EL}
\]

\[
E_{\text{cell}} = \frac{RT}{nF} \left( E^\circ_R + \frac{\ln C_2}{nF} \right) - \frac{RT}{nF} \left( E^\circ_L + \frac{\ln C_1}{nF} \right)
\]

\[
E_{\text{cell}} = \frac{(E^\circ_R - E^\circ_L) + RT}{RT} \left( \frac{\ln C_2}{nF} - \frac{\ln C_1}{nF} \right)
\]

\[
\therefore E_{\text{cell}} = \frac{2.303 \times RT}{nF} \frac{C_2}{\log C_1}
\]

or \( E_{\text{cell}} = \frac{0.0592 \times C_2}{\log C_1} \) at 25°C

There will be no current flow when the two solutions are at same concentration and when \( C_2/C_1 > 1 \) the reaction is spontaneous as \( E_{\text{cell}} \) is +ve.

Eg: An electrolyte concentration cell made up of Zinc dipping in two concentrations of Zinc sulphate \( C_1 \) and \( C_2 \) in such a way that \( C_2 > C_1 \). The cell can be represented as \( \text{Zn/Zn}^{2+} \_{(C1)} // \text{Zn}^{2+} \_{(C2)}/\text{Zn} \).

Cell reactions

Anode reaction, \( \text{Zn}_\text{(s)} \rightarrow \text{Zn}^{2+} \_{(C1)} + 2\text{e}^- \)

Cathode reaction \( \text{Zn}^{2+} \_{(C2)} + 2\text{e}^- \rightarrow \text{Zn}_\text{(s)} \)
Cell reaction \[ \text{Zn}^{2+}_{(C2)} \rightarrow \text{Zn}^{2+}_{(C1)} \]

**Applications**

i) Determination of valency of an ion

ii) To find out the solubility of sparingly soluble salts

iii) Determination of pH of a solution.

**POLARISATION**

Polarisation is a process in which there is a variation of electrode potential due to slow diffusion of ions from the bulk of the electrolyte solution to the vicinity of electrode or due to back emf brought about by the products of electrolysis.

Polarisation is of two types:

i) Concentration polarization

ii) Gas polarization

**Concentration polarization**

When a galvanic cell operates the concentration of ions surrounding the electrode differs from that in the bulk of the electrolyte. This change in concentration set up a back emf and the cell potential drops. This is known as concentration polarization which increase with time.

For example: Consider the Daniel cell for the relation is \( \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \). When current is drawn, concentration of Zn ions around the anode increases and that of copper
ions around the cathode decreases. Due to this change in concentration a back *emf* is produced and the *emf* of the cell falls down.

**Gas polarization**

This type of polarization may occur in electrolytic cells. This arises due to the formation of a resistant film of adhering atoms or molecules of gas on the electrode. This is known as gas polarisation which may occur when O\(_2\) or Cl\(_2\) is liberated at anode or H\(_2\) at cathode. The gas electrode thus formed produces an *emf* opposite to that of the cell.

**Factors affecting polarization**

1. Size of electrode- Large surface area decreases the polarization.
2. Nature of electrode- Rough surface decreases the polarization.
3. Concentration of electrolyte- Low concentration decreases the polarization.
4. Temperature- As the temp increases polarization decreases.
5. Depolarisers- Use of depolarizer decreases polarization. Example: M\(_n\)O\(_2\), HNO\(_3\), H\(_2\)CrO\(_4\) etc.

**Decomposition Potential**

When electrolysis is carried out, the products of electrolysis accumulate around the electrode. This results in a change in the concentration of the electrolyte around the electrode. This exert a back *emf* and hence the actual *emf* of the cell and finally electrolysis will stop.

For example: When a voltage is applied between two platinum electrodes dipped in acidified water, the electrolysis starts with the evolution of H\(_2\) and O\(_2\). But the electrolysis stops very soon, due to the back *emf* produced which is greater than applied
emf. If we increase the applied voltage slowly, the electrolysis well proceed smoothly when applied voltage exceeds the back emf.

Decomposition curve can be obtained by plotting current density against applied emf.

![Graph showing current density vs applied emf]

From the decomposition curve it is understood that the current density gradually increases with increase in applied emf. But at a particular stage there is a sudden increase in current density. The voltage at which there is a sudden increase in current density is known as decomposition potential.

The minimum potential or emf which must be applied between two electrodes immersed in a given electrolyte in order to overcome back emf due to polarisation and to bring about continuous electrolysis is known as decomposition potential. Thus decomposition potential is equal to back emf that is, Ed=Eb.

**Application of Decomposition Potential**
1. If a solution having a number of ions and is subjected to electrolysis, the ions will be discharged in the order of increasing decomposition potential. This fact is utilized in the separation of cautions.

2. The idea of decomposition potential is of great importance in electroplating.

3. In the refining of metals.

**Over voltage**

For carrying out continuous electrolysis, the applied voltage should at least overcome the back emf. In certain cases it is observed that electrolysis does not occur unless and until a potential much higher than the decomposition potential is applied.

Over voltage is defined as the difference between the potentials of the electrode at which electrolysis actually proceeds continuously and the theoretical decomposition potential.

**Factors affecting over voltage**

1. Nature of electrode.


3. Temperature.


5. PH of the electrolyte.

**Applications**

1. Due to high over voltage of Pb, which is only deposited on the cathode instead of H₂ being evolved during recharging in a lead acid accumulator.
2. In the electrolyte reduction of organic compounds.

3. Over voltage of $H_2$ makes it possible to deposit metals with more –ve potential than $H_2$ from acids.

**SECONDARY CELLS**

Secondary cells are those which can recharged again and again by passing direct current through them. This recharging makes them suitable for reuse. Example: lead-acid accumulator, Ni-Cd storage cell etc.

**Storage cells or Accumulators**

Storage cells are secondary cells in which electrical energy is stored as chemical energy from which electrical energy can be released when required. Example: Lead storage cell, Ni-Cd cell.

**Lead-Acid Accumulator (Lead Storage Battery)**

The most commonly used storage cell is Pb-acid storage cell. Each battery consists of 6 identical cells joined together in series. In each cell, the anode is a grid of Pb packed with finely divided spongy lead and the cathode is a grid of Pb packed with PbO$_2$. The lead plates are connected in parallel in an alternate fashion. Spongy lead acts as reducing agent and PbO$_2$ acts as oxidizing agent. The plates are separated from adjacent ones by using insulators. The electrolyte is a 20% solution of $H_2SO_4$ at 25$^0$C. The cell can be represented as Pb/$H_2SO_4$ (20%)/PbO$_2$, Pb.
The reversible reaction taking place in the cell can be written as \( \text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \) discharging \( 2\text{PbSO}_4 + 2\text{H}_2\text{O} \)

\[
\begin{align*}
\text{Discharging} & \\
\text{Recharging} & \\
\end{align*}
\]

\textbf{Discharging}

A storage cell is said to be discharging when it is supplying electrical energy. The cell reactions are spontaneous during the discharge process. The reactions are as follows:

\textbf{At anode}

\[
\begin{align*}
\text{Pb}_{(s)} & \rightarrow \text{Pb}^{2+}_{(aq)} + 2e^- \\
\text{Pb}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} & \rightarrow \text{PbSO}_4_{(s)}
\end{align*}
\]
\[
Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-
\]

**At cathode**

\[
PbO_2(s) + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O
\]

\[
Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)
\]

\[
PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O
\]

Cell reaction during discharging process is

\[
Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4(s) + 2H_2O
\]

A lead-acid storage cell is in use, both the electrodes get coated with white ppt of lead sulphate. The water produced in the reaction dilutes sulphuric acid. There by bringing down its density to 1.1 g/ml. When both the electrodes get covered with PbSO_4, the cell is said to be dead.

**Recharging**

During recharging, the cell operates as an electrolytic cell. To recharge an external emf greater than cell emf is passed when the reactions are reversed. The following reactions take place during recharging.

**At anode**

\[
PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^-
\]

**At cathode**

\[
PbSO_4 + 2e^- \rightarrow Pb(s) + SO_4^{2-}
\]

\[
2PbSO_4 + 2H_2O \rightarrow Pb(s) + PbO_2(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-}
\]
Due to high overvoltage of lead, it is only deposited on the cathode instead of H₂ being liberated at the cathode during recharging. The conc. H₂SO₄ increases during recharging.

**Nickel Cadmium Battery**

The *nickel-cadmium battery* (commonly abbreviated NiCd or NiCad) is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes.

**Construction and Working**

The basic construction of a nickel cadmium cell is depicted in Figure 4. Through my preliminary research, I found that the cells contain a positive nickel hydroxide electrode and a negative cadmium hydroxide electrode. The electrodes are electrically insulated by a separator, and potassium hydroxide (KOH) acts as the electrolyte. These components
are reeled into a jelly roll structure, and housed in a case. The chemical reaction of a nickel cadmium battery cell is described in the equation below:

\[ 2 \text{NiO(OH)} + \text{Cd} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Ni(OH)}_2 + \text{Cd(OH)}_2 \]

When the cell is being discharged, the reaction takes place from left to right. When it is being recharged, the reaction occurs from right to left

**Applications**

Sealed NiCd cells may be used individually, or assembled into battery packs containing two or more cells. Small NiCd dry cells are used for portable electronics and toys, often using cells manufactured in the same sizes as primary cells. When NiCds are substituted for primary cells, the lower terminal voltage and smaller ampere-hour capacity may reduce performance as compared to primary cells. Miniature button cells are sometimes used in photographic equipment, hand-held lamps (flashlight or torch), computer-memory standby, toys, and novelties.

Specialty NiCd batteries are used in cordless and wireless telephones, emergency lighting, and other applications. With a relatively low internal resistance, a NiCd battery can supply high surge currents. This makes them a favourable choice for remote-controlled electric model airplanes, boats, and cars, as well as cordless power tools and camera flash units. Larger flooded cells are used for aircraft starting batteries, electric vehicles, and standby power.

**Advantages**

When compared to other forms of rechargeable battery, the NiCd battery has a number of distinct advantages.
• The batteries are more difficult to damage than other batteries, tolerating deep discharge for long periods. In fact, NiCd batteries in long-term storage are typically stored fully discharged. This is in contrast, for example, to lithium ion batteries, which are less stable and will be permanently damaged if discharged below a minimum voltage.

• NiCd batteries typically last longer, in terms of number of charge/discharge cycles, than other rechargeable batteries.

• Compared to lead-acid batteries, NiCd batteries have a much higher energy density. A NiCd battery is smaller and lighter than a comparable lead-acid battery. In cases where size and weight are important considerations (for example, aircraft), NiCd batteries are preferred over the cheaper lead-acid batteries.

• In consumer applications, NiCd batteries compete directly with alkaline batteries. A NiCd cell has a lower capacity than that of an equivalent alkaline cell, and costs more. However, since the alkaline batteries chemical reaction is not reversible, a reusable NiCd battery has a significantly longer total lifetime. There have been attempts to create rechargeable alkaline batteries, such as the rechargeable alkaline, or specialized battery chargers for charging single-use alkaline batteries, but none that has seen wide usage.

• The terminal voltage of a NiCd battery declines more slowly as it is discharged, compared with carbon-zinc batteries. Since an alkaline batteries voltage drops significantly as the charge drops, most consumer applications are well equipped to deal with the slightly lower NiCd voltage with no noticeable loss of performance.

**Disadvantages**

The primary trade-off with NiCd batteries is their higher cost and the use of cadmium. They are more costly than lead-acid batteries because nickel and cadmium are more costly materials.
One of the NiCd's biggest disadvantages is that the battery exhibits a very marked negative temperature coefficient. This means that as the cell temperature rises, the internal resistance falls. This can pose considerable charging problems, particularly with the relatively simple charging systems employed for lead-acid type batteries. Whilst lead-acid batteries can be charged by simply connecting a dynamo to them, with a simple electromagnetic cut-out system for when the dynamo is stationary or an over-current occurs, the NiCd under a similar charging scheme would exhibit thermal runaway, where the charging current would continue to rise until the over-current cut-out operated or the battery destroyed itself. This is the principal factor that prevents its use as engine-starting batteries. Today with alternator-based charging systems with solid-state regulators, the construction of a suitable charging system would be relatively simple, but the car manufacturers are reluctant to abandon tried-and-tested technology.

**Lithium-MnO2 Cell**

There are three types of lithium batteries: Lithium Manganese Dioxide, which is a primary battery, and Lithium-Ion and Lithium-Ion-Polymer, which are secondary batteries.

The major advantages of lithium manganese batteries over alkaline batteries are their high energy and power density, good storage life and discharge performance. Lithium manganese batteries are found in a variety of shapes, with the most common being the button cells and the cylindrical batteries. The image at top right is a typical button cell or round lithium manganese battery.

Cylindrical lithium batteries are either solid-core (as at left) or wound (as at right). Additional information and a more detailed cutaway view are available by clicking on the image. Lithium primary batteries are available in a wide variety of electrochemical and physical configurations. They find use in cardiac pacemakers, in CMOS (complimentary metal-oxide-semiconductor) memory storage, powering LCD’s in watches, calculators and in other military and medical applications.
Their dependability and usefulness rests squarely on solid performance. Because of lithium manganese oxide's stability, these batteries can be stored for several years. Operating temperatures have little effect on operating characteristics because the cell is so efficient. Lithium batteries offer twice the voltage of other button cell batteries. And their small size, light weight, and high energy density make them perfect for applications that require high drain or pulse discharge over a broad temperature range. They also provide excellent performance at low temperatures, making them ideal for use in outdoor wireless weather devices. Also, storage life is outstanding because their self discharge is so very low.

Battery technologists have long been aware that lithium has the highest potential on the emf-scale as well as a low equivalent weight. This makes it a good anode candidate for a high-density battery, but it was not until a manufacturing process was developed to electroplate lithium for use as an anode that the lithium battery became a commercial product.

**Lithium Manganese Dioxide Battery Characteristics**

<table>
<thead>
<tr>
<th>Type</th>
<th>Primary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Reaction</td>
<td>( \text{Li + MnO}_2 \rightarrow \text{LiMnO}_2 )</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>-40º F to 140º F ( -40º C to 60º C). Best for extreme temperatures.</td>
</tr>
<tr>
<td>Recommended for</td>
<td>Outdoor use (requiring a low temperature range) and for high-discharge devices, which include (but are not limited to): digital cameras, RC cars, portable power tools, heavy-use flashlights, CB walkie-talkies, FRS radios, portable televisions, handheld video games, portable audio systems, CD players, MP3 players, appliances, shavers, and toothbrushes.</td>
</tr>
<tr>
<td>Initial Voltage</td>
<td>3.0 (button cell), 1.5 (cylindrical), 9 (rectangular)</td>
</tr>
<tr>
<td>Capacity</td>
<td>Varies</td>
</tr>
<tr>
<td>Discharge Rate</td>
<td>Flat</td>
</tr>
<tr>
<td>Internal Resistance</td>
<td>Low and stable</td>
</tr>
<tr>
<td>Impedance</td>
<td>Low and constant</td>
</tr>
<tr>
<td>Storage Life</td>
<td>Good shelf life; loses 0.5% per year.</td>
</tr>
</tbody>
</table>
Storage Temperature: -40º F to 140º F (-40º C to 60º C)
Disposal: Not recyclable
Lithium Ion Cell

A lithium-ion battery (sometimes Li-ion battery or LIB) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

Lithium-ion batteries are common in consumer electronics. They are one of the most popular for portable electronics, with one of the best energy-to-weight ratios, no memory effect, and a slow loss of charge when not in use. Beyond consumer electronics, LIBs are growing in popularity for military, electric vehicle, and aerospace applications due to their high energy density. Research is yielding a stream of improvements to traditional LIB technology, focusing on energy density, durability, cost, and safety.

Construction
The three primary functional components of a lithium-ion battery are the anode, cathode, and electrolyte. The anode of a conventional lithium-ion cell is made from carbon, the cathode is a metal oxide, and the electrolyte is a lithium salt in an organic solvent.

The most commercially popular anode material is graphite. The cathode is generally one of three materials: a layered oxide (such as lithium cobalt oxide), a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide).

The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions.\[^{10}\] These non-aqueous electrolytes generally use non-coordinating anion salts such as lithium hexafluorophosphate (LiPF\(_6\)), lithium hexafluoroarsenate monohydrate (LiAsF\(_6\)), lithium perchlorate (LiClO\(_4\)), lithium tetrafluoroborate (LiBF\(_4\)), and lithium triflate (LiCF\(_3\)SO\(_3\)).

Depending on materials choices, the voltage, capacity, life, and safety of a lithium-ion battery can change dramatically. Recently, novel architectures using nanotechnology have been employed to improve performance.

Pure lithium is very reactive. It reacts vigorously with water to form lithium hydroxide and hydrogen gas is liberated. Thus a non-aqueous electrolyte is typically used, and a sealed container rigidly excludes water from the battery pack.

**Electrochemistry**

The three participants in the electrochemical reactions in a lithium-ion battery are the anode, cathode, and electrolyte.

Both the anode and cathode are materials into which, and from which, lithium can migrate. During insertion (or intercalation) lithium moves into the electrode. During the reverse process, extraction (or deintercalation) lithium moves back out. When a lithium-based cell is discharging,
the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

Useful work can only be extracted if electrons flow through a closed external circuit. The following equations are in units of moles, making it possible to use the coefficient $x$. The cathode half-reaction (with charging being forwards) is:

$$\text{LiCoO}_2 \Leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$$

The anode half reaction is:

$$x\text{Li}^+ + xe^- + 6\text{C} \Leftrightarrow \text{Li}_x\text{C}_6$$

The overall reaction has its limits. Overdischarge supersaturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:

$$\text{Li}^+ + \text{LiCoO}_2 \rightarrow \text{Li}_2\text{O} + \text{CoO}$$

Overcharge up to 5.2 Volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction.

$$\text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{CoO}_2$$

In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in Li$_x$CoO$_2$ being oxidized from Co$^{3+}$ to Co$^{4+}$ during charging, and reduced from Co$^{4+}$ to Co$^{3+}$ during discharge.