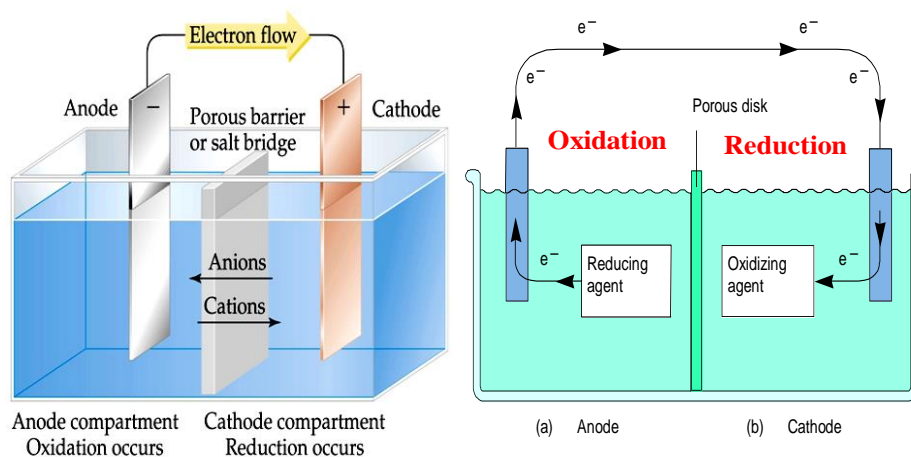


## 2. ELECTRICAL ENERGY SYSTEMS

**Syllabus:** Electrode potential, Nernst equation, formation of a cell; Reference electrodes—calomel electrode and determination of electrode potential; Numerical problems on  $E$ ,  $E_{\text{cell}}$  and  $E^0_{\text{cell}}$ . Batteries: classification, characteristics, lead-acid battery and lithium ion battery. Fuel cells: methanol- oxygen fuel cell.

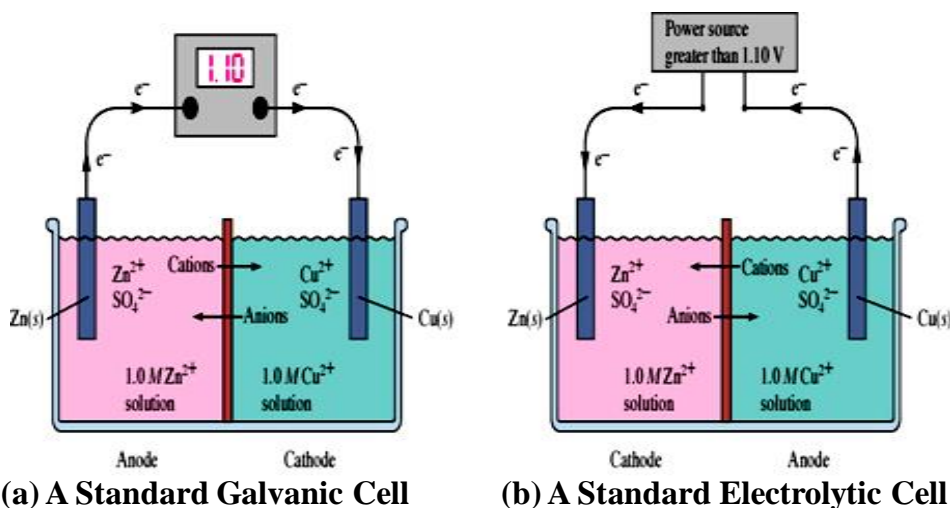
**Electrochemistry** is a branch of chemistry which deals with the study of transformation of chemical energy into electrical energy and vice versa (i.e., producing electrical energy from chemical reaction or bringing out chemical reactions by applying electrical energy). This chapter deals with a few fundamental concepts related with electrochemical cells.

**Electrochemical Cells:** “An electrochemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy by oxidation-reduction reaction”.



There are two types of Electrochemical cells.

1. Galvanic cell or voltaic cell: is the one, which converts chemical energy into electrical energy. Example- Dry cell, Lead-acid cell, Ni-Cd cell etc.
2. Electrolytic cell: is the one, which converts electrical energy into chemical energy.



**Single Electrode Potential (E):**

It can be defined as “the potential developed at the interface between the metal and solution, when it is in contact with a solution of its own ions”

OR

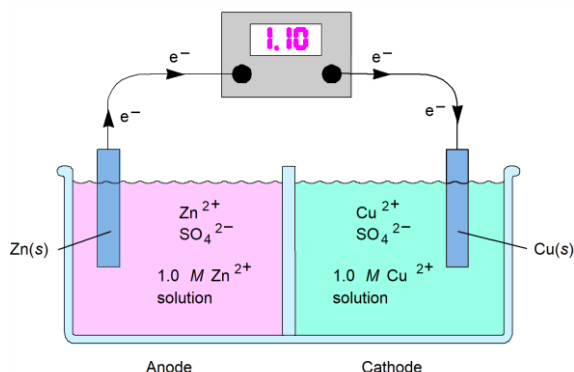
“Single electrode potential is a measure of tendency of a given half-cell reaction to occur as reduction, when it is in equilibrium with the other half cell”

**Standard reduction potential ( $E^\circ$ ):**

“Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration; at 298K. If the electrode involves a gas, then the gas should be at one atmosphere pressure”

**EMF or Cell potential:** The cell potential ( $E_{\text{cell}}$ ) or EMF of the cell is defined as the potential difference between two electrodes of a galvanic cell which causes the flow of current from an electrode with lower reduction potential to the electrode with higher reduction potential. The standard cell potential ( $E^\circ_{\text{cell}}$ ) of a galvanic cell is measured at standard conditions (298K, 1 M concentration, 1 atm pressure).

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

**NERNST EQUATION FOR SINGLE ELECTRODE POTENTIAL:**

Nernst equation gives a relationship between single electrode potential, standard electrode potential, concentration of metal ions and temperature.

In spontaneous redox reactions, the work done is equal to decrease in free energy. In such reactions, work done is the product of charge transferred ( $nF$ ) times the potential ( $E$ ).

$$-\Delta G = W_{\text{max}} \dots \dots \dots (1)$$

$$W_{\text{max}} = nFE \dots \dots \dots (2)$$

where,  $n$  = No. of moles of electrons,  $E$  = Electrode potential &  $F$  = Faraday's constant.

Under standard conditions,

$$-\Delta G^{\circ} = nFE^{\circ} \dots\dots\dots (3)$$

where,  $-\Delta G^{\circ}$  = Decrease in free energy under standard condition,  $E^{\circ}$  = Standard electrode potential

Consider a reversible electrode reaction



According to Van't Hoff's isotherm, the relationship between free energy change ( $\Delta G$ ) and equilibrium constant ( $K$ ) is given by,

$$\Delta G = \Delta G^{\circ} + RT \ln K \dots\dots\dots (5)$$

where,  $K$  = Equilibrium constant

$$\text{Since, } K = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{[M]}{[M^{n+}]}$$

Substitute the value of  $K$ ,  $\Delta G$  and  $\Delta G^{\circ}$  in equation (5)

$$-nFE = -nFE^{\circ} + RT \ln \left[ \frac{[M]}{[M^{n+}]} \right] \dots\dots\dots (6)$$

Divide the eqn (6) by ' $-nF$ ' and substitute  $\ln = 2.303 \log$  and  $[M] = 1$  (since the concentration of pure metal is taken as unity)

$$E = E^{\circ} - 2.303 \frac{RT}{nF} \log \left[ \frac{1}{[M^{n+}]} \right] \dots\dots\dots (7)$$

By rearranging the above equation, the Nernst equation for single electrode potential is obtained;

$$E = E^{\circ} + \frac{2.303RT}{nF} \log [M^{n+}] \dots\dots\dots (8)$$

Substitute gas constant ( $R$ ) = 8.314 J/K/mol, temperature ( $T$ ) = 298 K, Faraday's constant ( $F$ ) = 96500 C/mol in equation (8)

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}] \dots\dots\dots (9)$$

**Nernst equation for EMF of cell at 298K:**

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \left[ \frac{\text{Species at Cathode}}{\text{Species at Anode}} \right]$$

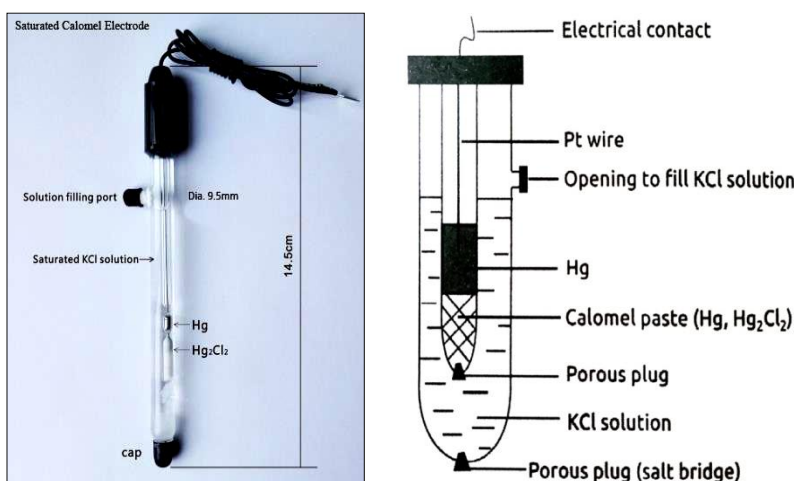
**REFERENCE ELECTRODES:** “Reference electrodes are with known electrode potential, with reference to which the electrode potential of any electrode can be measured”

There are two types of reference electrodes: Primary and Secondary Reference Electrode

**CALOMEL ELECTRODE:**

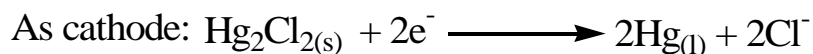
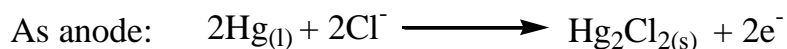
**Construction:** Calomel electrode is a secondary, metal-metal salt ion electrode. It consists of mercury, mercurous chloride and a solution of KCl. A paste of mercury and mercurous chloride is placed at the bottom of a glass tube. Mercury is placed above the mercury. The space in the glass tube is filled with a KCl solution of known concentration. A platinum wire is kept immersed into the mercury to obtain electrical contact.

Calomel electrode is represented as,  $\text{Hg}_{(l)} | \text{Hg}_2\text{Cl}_{2(s)} | \text{KCl}_{(aq)}$

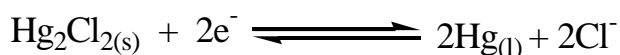


**Working:** Calomel electrode is a reversible electrode. It can act as anode or cathode depending on the nature of the other electrode of the cell.

The electrode reactions are,



The net reversible electrode reaction is,



Nernst equation for calomel electrode,  $E = E^0 - \frac{2.303RT}{nF} \cdot \log[\text{Cl}^-]^2$

$$E = E^0 - \frac{2.303RT}{F} \cdot \log[Cl^-] \quad \text{where } n=2$$

$$E = E^0 - 0.0591 \cdot \log[Cl^-] \quad \text{at } 298K$$

Calomel electrode is reversible with respect to  $Cl^-$  ions and the electrode potential of calomel electrode is decided by the concentration of KCl filled in it. Because the concentration of  $Cl^-$  is fixed by the solubility of KCl, the potential of an SCE remains constant even if we lose some of the solution to evaporation. A significant disadvantage of the SCE is that the solubility of KCl is sensitive to a change in temperature. At higher temperatures the solubility of KCl increases and the electrode's potential decreases. For example, the potential of the SCE is +0.2444 V at 25°C and +0.2376 V at 35°C. The potential of a calomel electrode containing an unsaturated solution of KCl is less temperature dependent, but its potential changes if the concentration, and thus the activity of  $Cl^-$  increases due to evaporation.

<u>KCl concentration</u>	<u>Electrode potential</u>
Saturated KCl (4.0 M)	0.242 V
1.0 M KCl	0.280 V
0.1 M KCl	0.334 V

#### **Applications:**

- It is used as secondary reference electrode in the measurement of single electrode potential.
- It is also used as reference electrode in all potentiometric quantitative analysis.

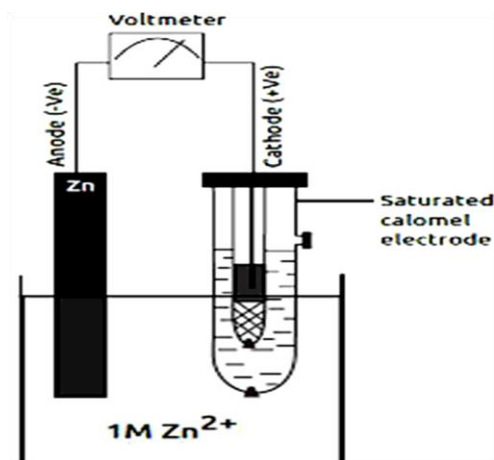
#### **Measurement of Standard Electrode Potential Using Calomel Electrode:**

Practically, it is not possible to measure the potential of single electrode. For this purpose calomel electrode is used. The potential of calomel electrode is assigned with respect to standard hydrogen electrode.

#### **Determination of standard electrode potential of Zn ( $E^0_{Zn}$ ):**

Zn rod is dipped in  $ZnSO_4$  solution and is connected to saturated calomel electrode through a voltmeter or potentiometer. The cell so formed may be represented as

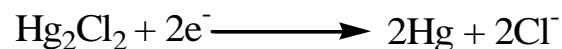




At anode, oxidation occurs,



At cathode, reduction occurs,



The standard EMF of the cell ( $E^{\circ}_{\text{cell}}$ ) is calculated using the equation:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

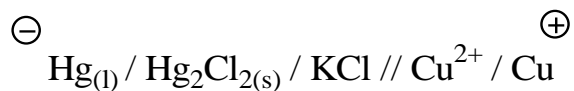
$$= E^{\circ}_{\text{SCE}} - E^{\circ}_{\text{Zn}}$$

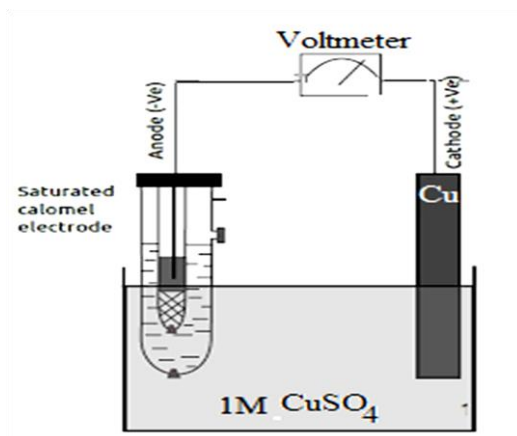
$$E^{\circ}_{\text{Zn}} = E^{\circ}_{\text{SCE}} - E^{\circ}_{\text{cell}}$$

$E_{\text{CE}}$  is known (0.2422) and  $E_{\text{cell}}$  (1.0022) is noted from voltmeter during EMF measurements. Using these values potential of Zn electrode (-0.76V) is measured.

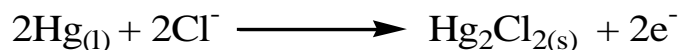
#### Determination of standard electrode potential of Cu ( $E^{\circ}_{\text{Cu}}$ ):

Cu rod is dipped in  $\text{CuSO}_4$  solution and is connected to saturated calomel electrode through a voltmeter or potentiometer. The cell so formed may be represented as,

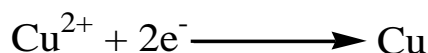




At anode, oxidation occurs,



At cathode, reduction occurs,



The standard EMF of the cell ( $E^\circ_{\text{cell}}$ ) is calculated using the equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= E^\circ_{\text{Cu}} - E^\circ_{\text{SCE}}$$

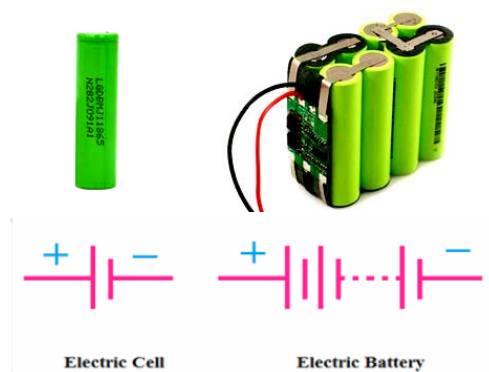
$$E^\circ_{\text{Cu}} = E^\circ_{\text{cell}} + E^\circ_{\text{SCE}}$$

$E_{\text{CE}}$  (0.2422) is known and  $E_{\text{cell}}$  (0.0978) is noted from voltmeter during EMF measurements. Using these values potential of Cu electrode (0.34V) is measured.

### BATTERY:

**A cell** designates a single unit made up of an anode and cathode, which produces potential i.e., the conversion of chemical energy into electrical energy, is a function of cells or batteries.

**A Battery** is a device which consists of more than two electrochemical cells connected in series or parallel that can be used as a source of direct electric current at a constant voltage. Hence, battery is a device that converts chemical energy contained in its active materials directly into electrical energy by means of an electrochemical redox reaction. In a battery, chemical energy (i.e., stored) is converted into electrical energy efficiently.

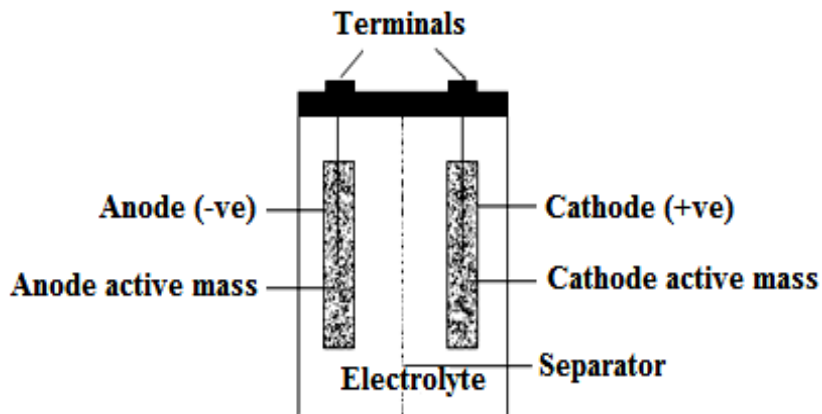


**Uses:** Batteries are used in calculators, watches and pacemakers for heart hearing aids, computers, car engines, standby power supplies, emergency lighting in hospitals, electroplating industrial tractions and military and space applications.

Batteries have revolutionized the telecommunication system and are ushering a new era of transportation with the possible replacement of petrol driven automobiles by the electrical powered ones. In modern days portability of electronic equipments in the form of handsets has been made possible by batteries.

### **BASIC COMPONENTS OF A BATTERY:**

The electrochemical unit in a battery is a galvanic cell or voltaic cell.



**Anode:** In a battery, anode is always negative terminal (or electrode) where oxidation takes place to release the electrons to the external circuit. In a rechargeable battery, it acts as positive terminal during charging. Zinc, lithium, cadmium, and lead are extensively used as anode material. Out of these, lithium tops the list because it readily gives off electrons (reduction potential is highest -3.05V). Zinc is the next obvious choice.

**Cathode:** It accepts the electrons readily which are generated at the anode and subsequently the active species getting reduced. It is +ve terminal of primary cell. During recharging it acts as an anode. Several types of cathode materials are used such as graphite rod, zinc, lead, nickel and cadmium. Sometimes both anode and cathode made up of same material like lead as in case of lead-acid battery.



**Electrolytes:** It is an ionic conductor that provides the ionic conductivity between anode and cathode of the battery. The electrolytes used are acids, salts or alkali having high ionic conductivity, and even solids can be used. It allows the ionic movement between the electrodes during charging & discharging. . Ex: NaCl, KOH, H<sub>2</sub>SO<sub>4</sub>, etc.

**Separator:** These are the permeable membrane that separates or isolates anode & cathode electrically to prevent internal short circuiting but transport of ions takes place between anode & cathode. Cellulose, vinyl polymers and polyolefin membranes are generally used as separators. Ex: cellulose, nafion membranes etc.

Cathode current collector, anode current collector, rubber seal and container are the minor components of battery.

Anode & cathode materials should satisfy the following conditions, so that they could be used for practical applications.

The Battery acts as voltaic cell i.e. oxidation takes place at the negative electrode (anode) and reduction takes place at the positive electrode (cathode).

During charging the Battery acts as an electrolytic cell. The current flow is reversed and oxidation takes place at the positive electrode (anode) and reduction takes place at the negative electrode (cathode).

### CLASSIFICATION:

Batteries are classified as primary and secondary and reserve batteries.

1. **Primary batteries:** In these batteries, chemical energy stored is converted to electrical energy spontaneously as long as active materials are present. These can be used only once because the chemical reactions that supply electric current are irreversible. The electrical current available depends on the quantity of active materials present. These are non-rechargeable batteries. Examples: Zinc-air battery, Zn-MnO<sub>2</sub> battery, etc.

2. **Secondary batteries:** These batteries can be recharged by passing electric current, because cell reactions are reversible. The redox reaction is reversed during recharging. Electrical energy is stored in the form of chemical energy in these batteries and used when needed. The charge-discharge cycle (cycle life) can be repeated several hundred times and these batteries can be built into giant generators with high capacities. Examples: Lead-acid battery, Nickel-Metal hydride battery, Nickel-Cadmium battery, Li-ion battery, etc.

Primary cells act only as galvanic cell, whereas, a secondary cell can act both as galvanic cell and electrolytic cell. During discharging it acts as galvanic cell converting chemical energy to electrical energy and during charging process it acts as electrolytic cell converting electrical energy to chemical energy.

**3. Reserve Batteries:** In this battery, one of the key components is stored separately, and is incorporated into battery when required. This reduces the self discharge of the battery. When long storage is required, reserve batteries are often used. Examples: Mg-AgCl battery is activated by adding sea water. These batteries find applications in missiles and submarines because of their long shelf life and high capacity.

### **BATTERY CHARACTERISTICS:**

**1. Voltage (or) EMF:** The EMF of the battery depends on the total number of cells present in a battery and potential difference between electrodes of each cell. It also depends on the free energy changes in the overall cell reaction.

As given by Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

From above equation, it is clear that EMF of the cell depends on  $E^{\circ}_{\text{cell}}$ . More the number of cells, higher is EMF and efficient is the battery. Similarly, higher the potential difference between electrodes of each cell, higher is the EMF of the cell and efficient is the battery i.e.,  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ .

**2. Current:** Current is a measure of the rate at which the battery is discharging. Higher the rate of spontaneous reaction, higher is the current. Higher the surface area of the electrodes, higher is the rate of reaction. For an efficient working of the cell there must be a large quantity of electro active species that help rapid electron transfer reaction.

**3. Capacity:** Capacity is a measure of the amount of electricity that may be obtained from the battery. It is expressed in Ah (ampere hours) and it depends on the size of the battery. It is proportional to the amount of charge in Coulombs that may be transported from anode to cathode through the external circuit. The charge (C) in Coulombs is given by the Faraday's relation:

$$C = \frac{(W \times n \times F)}{M}$$

where W is the weight of active material present at one of the electrodes, n = number of electrons involved in discharge reaction, F = 96500 C/mol, and M its molar mass. The amount of the active material actually consumed during discharge determines the capacity of battery

**4. Power density:** It is power per unit weight of the battery. Power density decreases during discharging. It depends on quantity of active materials present in the cell.

$$\text{Power density} = \frac{\text{Power produced by cell}}{\text{Unit weight of the cell}}$$

**5. Electricity storage density:** It is the amount of electricity stored in the battery per unit weight of the battery i.e. it is the capacity per unit weight. It can be expressed in Coulombs/kg or in Ah/kg. The weight includes the weight of all components of the battery (i.e. total weight of active material, electrolyte, terminals etc.)

**6. Energy efficiency:** The energy efficiency of a rechargeable battery is given by

$$\% \text{ Energy efficiency} = \frac{\text{Energy released during discharge} \times 100}{\text{Energy consumed during charging}}$$

Higher the energy efficiency, very good is the battery

**7. Cycle life:** It is the number of discharge – charge cycles possible in a rechargeable battery before failure occurs. A good battery must have high cycle life.

**8. Shelf life:** It is the measure of storage capacity (storage duration) of a battery without self discharge. A good battery must have long shelf life.

**9. Tolerance to service condition:** The battery should be tolerant to service conditions like variation in temperature & vibration.

## **CONSTRUCTION, WORKING AND APPLICATIONS OF BATTERIES**

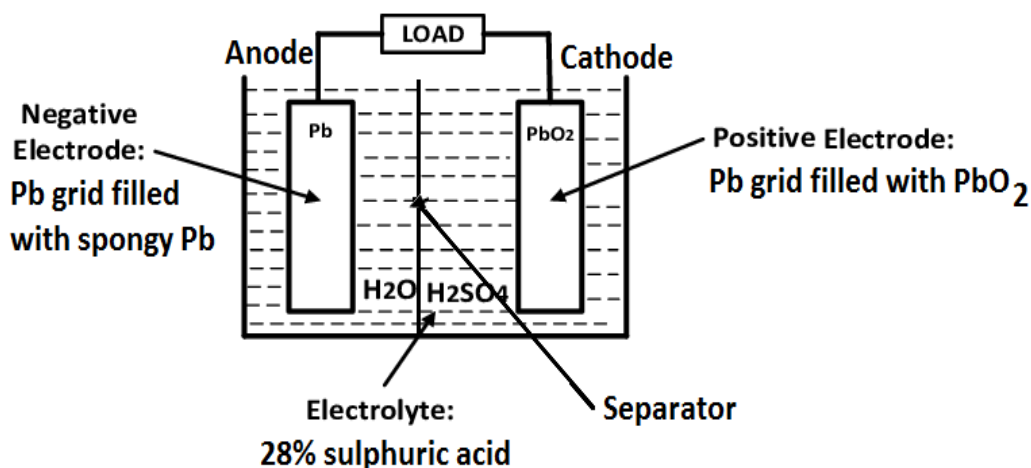
### **LEAD-ACID BATTERY:**

**Construction:** A single unit cell of Pb-acid battery uses following materials.

Anode: Lead (Pb) is the active material at anode

Cathode: Lead oxide (PbO<sub>2</sub>)

Electrolyte: 28% H<sub>2</sub>SO<sub>4</sub> with specific gravity equal to or more than 1.2.



Specific gravity= density of material/density of water

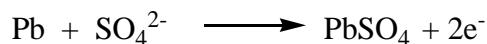
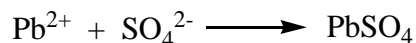
Density= -----g/cm<sup>3</sup> or kg/m<sup>3</sup>

In a container, 28% of H<sub>2</sub>SO<sub>4</sub> electrolyte is poured and then a lead grid filled with spongy lead and a lead grid filled with lead oxide is suspended in the electrolyte. Electrode with spongy lead acts as anode. Electrode with lead oxide acts as cathode. A separator can be placed between anode and cathode which will not allow the transportation of cations and anions across the electrolytes. One such cell can produce 2.04V of electrical energy as long as specific gravity of H<sub>2</sub>SO<sub>4</sub> is 1.2 or more.

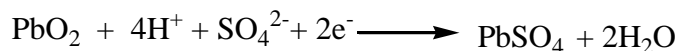
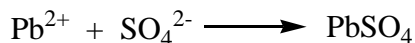
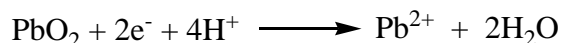
**Working:** Battery being secondary works in two cycles i.e., discharging and charging cycle.

**During discharging cycle:**

**Anode:**

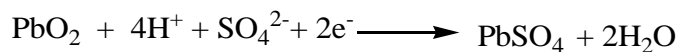


**Cathode:**



**Anode:**



**Cathode:****During charging cycle:**

After discharging, lead and lead oxide, the active materials at anode and cathode are converted into lead sulphate which gets deposited on the electrodes. Also concentration and specific gravity of  $\text{H}_2\text{SO}_4$  decreases which in turn reduces the total output of the battery. Now the battery can be charged by supplying external current.

**Applications:**

- Used in automobiles for starting and lighting
- For railway trains lighting
- Used at generating station to operate protective devices
- Used in telephone exchanges
- Used in emergency tube lights
- Used for lighting purposes in remote rural areas.

**LITHIUM CELLS**

Lithium metal is attractive as a battery anode material because of its lightweight, high voltage, high electrical equivalence and good conductivity, superior shelf life, Operation over a wide range of temperature. Sony introduced lithium battery in 1991. These are classified as primary and secondary cells.

**Li-MnO<sub>2</sub> cell:**

**Construction:** Li-MnO<sub>2</sub> is a primary battery and is not chargeable.

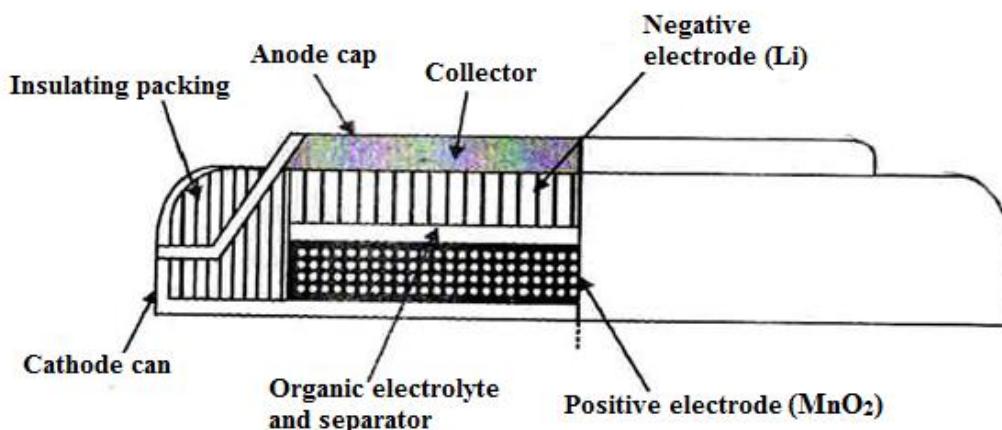
**Anode:** The anode is made of lithium metal.

**Cathode:** The cathode is made of MnO<sub>2</sub>.

**Electrolyte:** A solution of lithium halide dissolved in organic solvent acts as the electrolyte.

**Separator:** The anode and cathode are separated by a non-woven polypropylene separator.

The cell is sealed with the can serving as the positive terminal and the cap as the negative terminal.

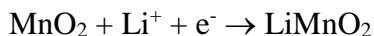


**Working:** Cell reaction during discharge,

**At anode:** lithium undergo oxidation



**At cathode:**  $\text{MnO}_2$  reduces from tetravalent to trivalent state by lithium



**Overall reaction:** On discharge is,  $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$

**Voltage:** The cell potential is 3 - 3.5 volts.

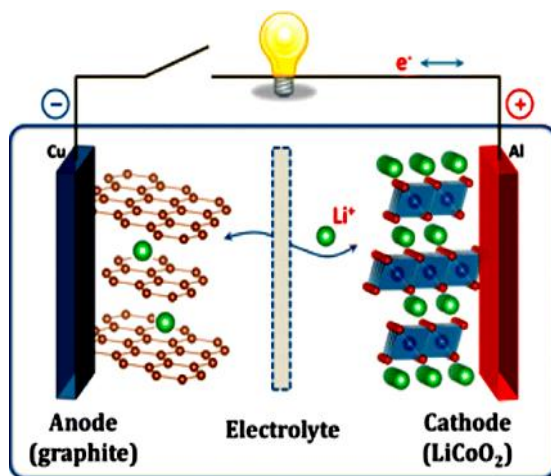
Once all the lithium and  $\text{MnO}_2$  are consumed and converted into  $\text{LiMnO}_2$ , battery stops producing electrical energy and must be replaced with a new battery.

**Applications:** Used as long-term memory backup, safety and security devices, cameras, calculators, cardiac pacemakers, hearing aids, lighting equipment and many consumer electronic devices.

## LITHIUM ION BATTERIES

Rechargeable battery best suited to mobile devices that require small size light weight and high performance. These include high voltage, high energy density, high cycle life and very low self-discharge when not in use. It provides maximum voltage of 3.7 V after complete charge. The battery consists of a anode of lithium, dissolved as ions into a carbon. The cathode material is made up of lithium liberating compounds such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiNiO}_2$ .

**Construction:** Lithium-ion batteries are composed of three parts: anode, cathode and electrolyte. Anode and cathodes are able to insert lithium ions into their layered structure reversibly.



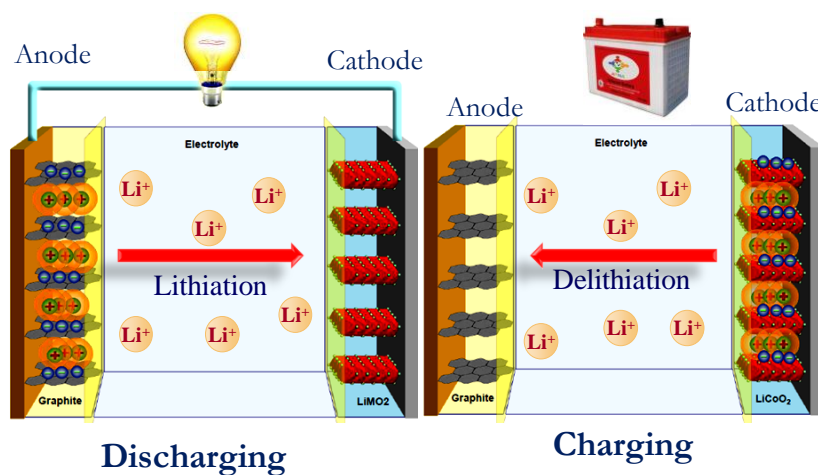
**Anode:** lithium intercalated graphite/carbon with copper foil as current collector.

**Cathode:** Lithium-metal oxide ( $\text{Li-MO}_2$ ), where M is commonly Co or Mn with aluminium foil as current collector.

**Electrolyte:**  $\text{LiPF}_6$  in organic solvent (i.e., Solid lithium-salt electrolyte  $\text{LiPF}_6$  or  $\text{LiBF}_4$  and organic solvent)

**Separator:** Micro porous polyethylene / fine porous polymer film.

**Working:** During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery. Simply, the Li-ion is transferred between anode and cathode through lithium electrolyte.



### Cell reactions during discharge and recharge process:

In lithium-ion battery, lithium ions move from the anode to the cathode during discharge and are intercalated into, i.e., are inserted into, open spaces in the voids in the cathode. The lithium ions make the reverse journey during charging.

The lithium ions are transported to and fro from the anode or cathode, by reducing the transition metal, cobalt in  $\text{LiCoO}_2$  from  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  during discharge and by oxidizing the transition metal, cobalt in  $\text{Li}_2\text{CoO}_2$  from  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  during charge.

### **WORKING:**

The electrode reactions that occur during **discharge process** of the cell that is when current is drawn from the cell are:

At anode:  $\text{LiC}_6 \rightarrow \text{C}_6 + \text{Li}^+ + \text{e}^-$

At cathode:  $\text{LiCoO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{Li}_2\text{CoO}_2$

Overall battery reaction:  $\text{LiC}_6 + \text{LiCoO}_2 \rightarrow \text{C}_6 + \text{Li}_2\text{CoO}_2$

The electrode reactions that occur during **charge process** of the battery are:

Reaction at the **negative terminal** [cathode]:  $\text{C}_6 + \text{Li}^+ + \text{e}^- \longrightarrow \text{LiC}_6$

Reaction at the **positive terminal** [anode]:  $\text{Li}_2\text{CoO}_2 \longrightarrow \text{LiCoO}_2 + \text{Li}^+ + \text{e}^-$

The **net reaction** during **charging process** is:  $\text{C}_6 + \text{Li}_2\text{CoO}_2 \longrightarrow \text{LiC}_6 + \text{LiCoO}_2$

**Voltage:** The cell potential is around 3.85 - 4.2 volts.

### **Advantages:**

- High energy density
- Long life
- High cell voltages
- Low self-discharge
- Wide range of temperature

**Note:** Lithiated graphite, like pure lithium, reacts vigorously with water to form lithium hydroxide ( $\text{Li-OH}$ ) and hydrogen gas. Thus, a non-aqueous electrolyte (lithium hexafluoro phosphate,  $\text{LiPF}_6$  dissolved in organic solvent such as ethylene carbonate) is typically used.

**Applications:** These are currently used for powering portable electronic devices like cell phones, cameras, calculators, laptop computers and also in defense, electrical vehicles, power tools and aerospace applications.



## FUEL CELLS

Fuel cells are galvanic cells used to convert chemical energy of fuel into electric current by direct oxidation of fuel at anode and reduction of oxidant at cathode. A fuel cell consists of two electrodes and an electrolyte. Fuel and oxidant are supplied from outside continuously and electrical energy is obtained as long as these react at electrodes.

A fuel cell may be represented as,

Fuel | anode | electrolyte | cathode | oxidant

### Advantages of fuel cells:

- The fuel cells operate very silently.
- Energy conversion rate is high.
- Produce harmless byproducts.
- Maintenance is less, space required is less.
- No need of charging.
- Have high energy density.

### Limitations:

- Power output is moderate.
- Electrodes are very costly.
- Fuels are to be stored in tanks under very high pressure.
- Gives DC output and should be converted to AC.

### Differences between a battery and a fuel cell

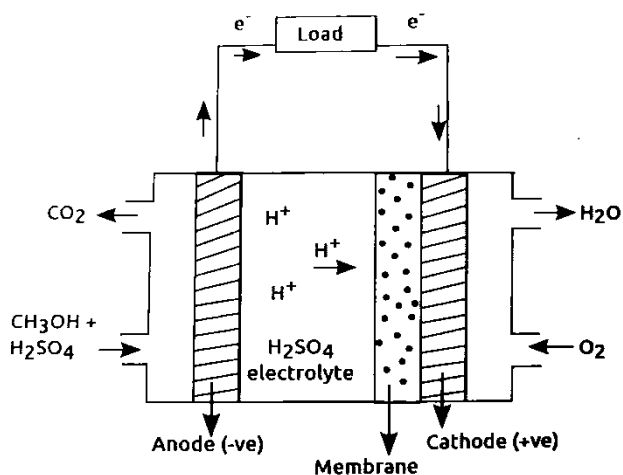
Batteries	Fuel cells
<ol style="list-style-type: none"> <li>1. The active materials are mixture of complex chemical composition.</li> <li>2. Create chemical pollution in the atmosphere.</li> <li>3. Recharging of the batteries is required.</li> <li>4. Electrodes are relatively cheaper.</li> <li>5. Active materials are placed along with electrodes in the cell.</li> <li>6. The electrodes are not assisted with catalysts.</li> <li>7. In some cases electrodes are consumed during production of energy.</li> </ol>	<ol style="list-style-type: none"> <li>1. The active materials are fuel and oxidant.</li> <li>2. Less harmful byproducts are discharged to atmosphere.</li> <li>3. Recharging of the fuel cells is not required.</li> <li>4. Electrodes are very costly.</li> <li>5. Active materials are stored outside the cell and are supplied whenever required.</li> <li>6. The electrodes are impregnated with catalysts.</li> <li>7. The electrodes are not consumed during production of energy.</li> </ol>

### METHANOL – OXYGEN FUEL CELL:

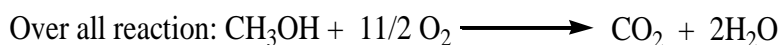
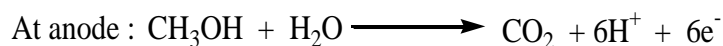
This fuel cell uses either alkaline or acidic medium. Use of acidic medium is found to be efficient. Also, methanol is relatively cheap and easily available fuel with less carbon content. It has got easily oxidizable – OH group.

**Construction:**

- The anode and cathode are porous nickel sheets coated with electro catalysts.
- Platinum/Ruthenium catalyst is coated on anode and Platinum alone is coated on cathode.
- Electrolyte 3.7M H<sub>2</sub>SO<sub>4</sub> is placed in the central compartment.
- Methanol mixed with H<sub>2</sub>SO<sub>4</sub> is passed through the anode chamber as a fuel.
- Pure oxygen is passed through the cathode chamber as oxidant.
- To prevent the diffusion of anode reactant methanol into cathode chamber, a proton conducting membrane is placed near cathode.



**Working:** At anode the oxidation of methanol on a catalyst layer forms carbon dioxide. Protons released are transported across the proton exchange membrane to the cathode where they react with oxygen to produce water. During the process, electrons are flowing through an external circuit from anode to cathode, provides power to connected devices.

**Cell reactions:**

**Voltage:** The cell potential is 1.2 volts.

**Applications:** It is used in military applications and large-scale power productions. It is also used in fuel cell vehicles and space shuttles.

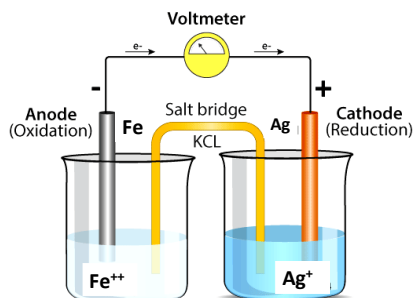
**Advantages:** Low cost liquid fuel. No reforming step for fuel.

**Disadvantages:** Slow reaction. The fuel cell requires membrane to avoid diffusion of fuel from anode to cathode.

**Note:** KOH is not used as electrolyte as it reacts with  $\text{CO}_2$  and gets converted to  $\text{K}_2\text{CO}_3$ . Thus conductivity of the electrolyte decreases as well as the efficiency. The advantage of acid electrolyte is that the  $\text{CO}_2$ , a product of the reaction can be easily removed.

### NUMERICAL PROBLEMS ON NERNST EQUATION

1) Calculate the emf of the cell  $\text{Fe} \mid \text{Fe}^{++}_{(0.01)} \parallel \text{Ag}^{+}_{(0.1)} \mid \text{Ag}$  at 298K if standard electrode potentials of Fe and Ag electrodes are  $-0.42$  and  $0.8$  V respectively.



**Cell reactions:** At anode:  $\text{Fe}_{(s)} \rightarrow \text{Fe}^{++}_{(aq)} + 2e^-$

At cathode:  $2\text{Ag}^{+}_{(aq)} + 2e^- \rightarrow 2\text{Ag}_{(s)}$

Net cell reaction:  $2\text{Ag}^{+}_{(aq)} + \text{Fe}_{(s)} \rightarrow \text{Fe}^{++}_{(aq)} + 2\text{Ag}_{(s)}$

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= E^0_{\text{Ag}} - E^0_{\text{Fe}}$$

$$= 0.8 - (-0.42)$$

$$E^0_{\text{cell}} = 1.22 \text{ V}$$

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Fe}^{++}]}$$

$$= 1.22 + \frac{0.0591}{2} \log_{10} \frac{(0.1)^2}{(0.01)}$$

$$= 1.22 + 0.02955 \log (1)$$

$$\underline{E_{\text{cell}} = 1.22 \text{ V}}$$

2) A cell is constructed by coupling Zn electrode dipped in  $0.5M$   $\text{ZnSO}_4$  and Ni electrode dipped in  $0.05M$   $\text{NiSO}_4$ . Write the cell representation, cell reaction. Calculate the EMF of cell, given that reduction potential of Zn and Ni as  $-0.76$  and  $-0.25$  volt respectively.



**Cell representation:**  $\text{Zn} \mid \text{ZnSO}_4(0.5M) \parallel \text{NiSO}_4(0.05M) \mid \text{Ni}$ .

**Cell reactions:** At anode:  $\text{Zn}_{(s)} \rightarrow \text{Zn}^{++}_{(aq)} + 2e^-$

At cathode:  $\text{Ni}^{++}_{(aq)} + 2e^- \rightarrow \text{Ni}_{(s)}$

**Net cell reaction:**  $\text{Zn}_{(s)} + \text{Ni}^{++}_{(aq)} \rightarrow \text{Zn}^{++}_{(aq)} + \text{Ni}_{(s)}$

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= E^0_{\text{Ni}} - E^0_{\text{Zn}}$$

$$= -0.25 - (-0.76)$$

$$E^0_{\text{cell}} = 0.51 \text{ V}$$

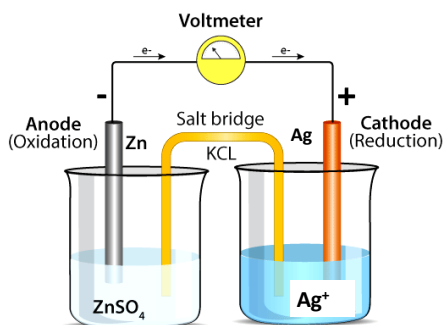
$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Ni}^{++}]}{[\text{Zn}^{++}]}$$

$$= 0.51 + \frac{0.0591}{2} \log_{10} (0.05)$$

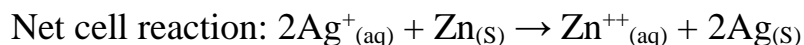
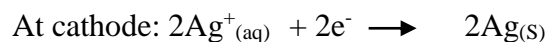
$$= 0.51 + 0.02955 \log (0.1)$$

$$\underline{E_{\text{cell}} = 0.4805 \text{ V}}$$

3) Calculate the potential of Ag – Zn cell at 298 K if the concentrations of  $\text{Ag}^+$  and  $\text{Zn}^{++}$  are  $5.2 \times 10^{-6} \text{ M}$  and  $1.3 \times 10^{-3} \text{ M}$  respectively.  $E^0$  of the cell at 298K is 1.5 V. Calculate the change in free energy  $\Delta G$  for the reduction of 1 mole  $\text{Ag}^+$ . 1 faraday = 96.5 k J/ V/mole.



**Cell reactions:** At anode:  $\text{Zn}_{(s)} \rightarrow \text{Zn}^{++}_{(aq)} + 2e^-$



$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Zn}^{++}]}$$

$$= 1.5 + \frac{0.0591}{2} \log_{10} \frac{(5.2 \times 10^{-6})^2}{(1.3 \times 10^{-3})}$$

$$= 1.5 + 0.02955 \log (20 \times 10^{-9})$$

$$E_{\text{cell}} = 1.2729 \text{ V}$$

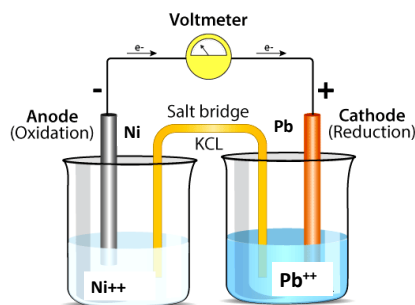
For the reduction of 2 moles of  $\text{Ag}^+$  ions, 2 electrons are required for the reduction of 1 mole of  $\text{Ag}^+$  ions, 1 electron is required.

$$\Delta G = -n F E_{\text{cell}}$$

$$= -1 \times 96.5 \times 1.2729$$

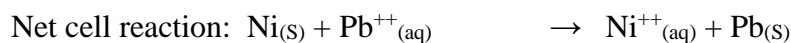
$$\Delta G = -122.83 \text{ KJ / mol}$$

- 4) A cell is constructed by coupling Ni electrode dipped in 0.01M  $\text{NiSO}_4$  and Pb electrode dipped in 0.5M  $\text{PbSO}_4$ . Write the cell representation, cell reactions. Calculate the EMF of cell, given that reduction potentials of Ni and Pb are  $-0.24$  and  $-0.13$  volt respectively.



**Cell representation:**  $\text{Ni}_{(\text{s})} | \text{Ni}^{++}_{(0.01\text{M})} || \text{Pb}^{++}_{(0.5\text{M})} | \text{Pb}_{(\text{s})}$

**Cell reactions:**



$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= E^0_{\text{Pb}} - E^0_{\text{Ni}}$$

$$= -0.13 - (-0.24)$$

$$E^0_{\text{cell}} = 0.11 \text{ V}$$

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Pb}^{++}]}{[\text{Ni}^{++}]}$$

$$= 0.11 + \frac{0.0591}{2} \log_{10} \frac{(0.5)}{(0.01)}$$

$$= 0.11 + 0.02955 \log (50)$$

$$\underline{E_{\text{cell}} = 0.1602 \text{ V}}$$

**5) Calculate the EMF of the cell  $\text{Zn}|\text{Zn}^{2+}_{(0.1\text{M})}||\text{Ag}^{+}_{(0.2\text{M})}|\text{Ag}$ . Given the standard electrode potentials of zinc and silver electrodes are -0.76V and 0.80V respectively.**

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= E^0_{\text{Ag}} - E^0_{\text{Zn}}$$

$$= 0.80 - (-0.76)$$

$$E^0_{\text{cell}} = 1.56 \text{ V}$$

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Zn}^{++}]}$$

$$= 1.56 + \frac{0.0591}{2} \log_{10} \frac{(0.2)^2}{(0.1)}$$

$$= 1.56 + 0.02955(-0.3979)$$

$$= 1.56 - 0.1175$$

$$\underline{E_{\text{cell}} = 1.54825 \text{ V}}$$

**6) Calculate the reduction electrode potential of copper when it is in contact with 0.5M copper sulfate solution at 298K. The  $E^0$  value of copper is 0.34V.**

$$E = E^0 + \frac{0.0591}{n} \log_{10} [\text{M}^{n+}]$$

$$E = 0.34 + \frac{0.0591}{2} \log_{10} (0.5)$$

$$E = 0.34 + 0.0295 (-0.3010)$$

$$\underline{E = 0.3311 \text{ V}}$$