

Department of Chemistry

ENGINEERING CHEMISTRY, 24ECHB102 UNIT 2 - CHAPTER 6: Energy Storage and Conversion Systems

Electrochemistry

Electrochemistry is a branch of science which deals with the transformation of chemical energy into electrical energy and vice-versa through oxidation reduction reactions. Because of the practical importance of electrochemistry, it has become a very interesting field of study for scientists and technologists.

An important aspect of electrochemistry is the inter conversion of electrical energy and chemical energy that takes place through oxidation – reduction reactions. Redox reactions form the basis of electrochemical cells.

Oxidation:

In oxidation, a species loses one or more electrons resulting in an increase in the oxidation number.



Reduction:

In reduction, a species gains one or more electrons resulting in a decrease in the oxidation number.



A substance cannot lose electrons unless another substance which can gain electrons is also present in its environment. Such an arrangement exists in electrochemical cells.

Single Electrode potential, E:

It is defined as the potential developed on the electrode at the interface between the metal and the solution when the electrode is in contact with a solution of its own ions.

(or)

The single electrode potential is a measure of the tendency of a given half-cell reaction to occur as reduction when it is in equilibrium with the other half-cell.

Standard Electrode potential, E^o:

It is defined as the potential developed on the electrode at the interface between the metal and the solution when the electrode is in contact with a solution of its own ions of unit concentration at 298K. If the electrode involves a gas, then the gas is at 1 atmospheric pressure.

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Electromotive Force of the cell, E_{cell} :

The potential difference between the two electrodes of a galvanic cell which causes the flow of current from one electrode of higher potential to the other electrode of lower potential is called the electromotive force (*emf*) of the cell or cell potential.

The *emf* of a cell represents the driving force of a cell reaction. As represented by the thermodynamic relation,

$$\Delta G = -nFE$$

where ΔG is the free energy change accompanying a cell reaction, n is the number of electron transfer during the cell reaction and F is Faraday.

The cell reaction is spontaneous or feasible when ΔG is negative.

Standard Electromotive Force of the cell, E°_{cell} :

Standard emf of a cell is defined as the emf of a galvanic cell when the reactants and products of the cell reaction are at unit concentration at 298K and at 1 atmospheric pressure.

Electrochemical cells:

An electrochemical cell consists of two electrodes which when connected by a metallic wire, an electric current flows as a result of a spontaneous redox reaction. Each electrode usually consists of a metal in contact with a solution of its own ions.

Since a cell is a combination of two electrodes, each electrode is referred to as a single electrode or half-cell.

A potential called the Electrode potential arises at the electrode in contact with its ionic solution. The difference between the potentials of the two half-cells constitutes the electromotive force (*emf*) of the cell.

Thus an **Electrochemical cell** is a device which converts chemical energy into electrical energy or electrical energy into chemical energy.

Electrochemical cells are of two types.

- The one which converts chemical energy into electrical energy - the so called galvanic cell or voltaic cell.
- The one which converts electrical energy into chemical energy – the so called electrolytic cell.

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Nernst Equation for single electrode potential of an electrode

In the year 1889 German chemist named Walther Hermann Nernst derived a quantitative relationship between the electrode potential and concentration of the electrolyte species involved.

Consider the following reversible electrode reaction: $M^{n+} + ne^- \rightarrow M$

By convention, the electrode reaction is written with reduction reaction in the forward direction, as electrode potential is the measure of reduction tendency.

The decrease in free energy change, ΔG , accompanying the process is given by the well-known thermodynamic equation:

$$-\Delta G = -\Delta G^\circ - RT \ln K \quad \dots \quad (1)$$

where ΔG° is the decrease in free energy change accompanying the same process when the reactants and products of the reaction are in their standard states of unit activity; K stands for reaction quotient of the activities of the products and reactants at any given stage of the reaction.

$$K = a_M / a_{M^{n+}}$$

Substituting the value of K , we get,

$$-\Delta G = -\Delta G^\circ - RT \ln(a_M / a_{M^{n+}}) \quad \dots \quad (2)$$

According to Von't Hoff reaction isotherm,

$$a_M = V [M] \text{ and } a_{M^{n+}} = V [M^{n+}]$$

where V is activity coefficient and as an approximation, let $V = 1$.

$$\text{Now, } a_M = [M] \text{ and } a_{M^{n+}} = [M^{n+}]$$

Now, by substituting the molar concentration for activities in equation (2) we get,

$$-\Delta G = -\Delta G^\circ - RT \ln([M]/[M^{n+}]) \quad \dots \quad (3)$$

The maximum work obtained from a chemical reaction is given by $-\Delta G = W_{max}$

For an electrochemical cell, the maximum work done is useful electrical work. Thus, $W_{max} = nFE$

Where, ' E ' is the electrode potential of the electrode in volts and the electrode reaction involves transfer of ' n ' electrons, i.e., nF coulombs. Hence, the electrical work available from the electrode is equal to nFE volt coulombs or Joules.

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Hence, free energy decrease of the system, ΔG and standard free energy decrease of the system, ΔG° is given by the expression:

$$-\Delta G = nFE \text{ and } -\Delta G^\circ = nFE^\circ$$

Now the equation (3) will be

$$nFE = nFE^\circ - RT \ln([M]/[M^{n+}]) \quad \dots \quad (4)$$

Divide the equation by nF.

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

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}] \text{ since } [M] = 1.$$

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \text{ volts} \quad \dots \quad (5)$$

where E° is the standard electrode potential, R is the Universal gas constant, T is absolute temperature and F is Faraday.

When the values of R = 8.314 J/K-Mole, F = 96,500 coulombs and T = 298K are substituted, the Nernst equation (5) will be

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \text{ volts} \quad \dots \quad (6)$$

The Nernst equation can also be applied for the calculation of *emf* of the cell. That is, the Nernst equation provides a relation between the cell potential of an electrochemical cell, the standard cell potential, temperature and the reaction quotient.

Consider the cell reaction, $aA + bB \rightarrow cC + dD$

The Nernst equation for the emf of the cell is

$$E_{cell} = E_{cell}^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ volts} \quad \dots \quad (7)$$

Where, E_{cell} = cell potential of the cell, E_{cell}° = cell potential of the cell under standard conditions and n = number of electrons transferred in the redox reaction.

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ELECTROCHEMICAL CONVENTIONS

(1) Sign of the electrode potential:

According to latest convention adopted by **IUPAC**, the electrode potential is given a positive sign if the electrode reaction involves reduction when connected to the standard hydrogen electrode and a negative sign if the electrode reaction involves oxidation when connected to the standard hydrogen electrode taken arbitrarily as zero.

Thus, when copper electrode is connected with a standard hydrogen electrode, reduction takes place at the copper electrode. Hence, according to above convention, the potential of copper electrode is taken as positive.

However, if zinc electrode is connected with a standard hydrogen electrode, oxidation takes place at the zinc electrode. Hence, according to above convention, the potential of zinc electrode is taken as negative.

(2) Representation of an electrode:

If an electrode acts as anode, i.e., if oxidation takes place at the electrode, the electrode is represented as



Here the convention is that, we have metal atoms first which later become metal ions as given by equation:

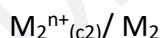


The vertical line represents the fact that the metal atoms and ions are in different phases. The term inside the bracket (c_1) represents the concentration of the metal ion.

If reduction takes place at the electrode, then the reaction is



Using the above convention, this electrode can be represented as:



Here, we have the ions first and then on reduction they become atoms.

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(3) Representation of a cell:

If two electrodes are combined to form a cell, then the cell is represented by writing the electrode conventions side by side with the anode on the left and the cathode on the right. The two electrode representations are separated by a double line. The double line represents the presence of a salt bridge. Hence, the cell can be represented as:

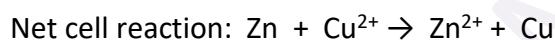
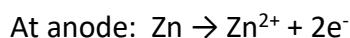


For example, the Daniel cell can be represented as follows:



(4) Writing electrode reactions and cell reaction:

The cell reaction is the sum of the electrode reactions as they occur in the cell. At the anode oxidation takes place and at the cathode reduction is the electrode reaction. For example, in Daniel cell,



The cell reaction is spontaneous when the *emf* of the cell is positive. This can be understood from the relation, $\Delta G = -nFE_{cell}$

For spontaneity of a reaction, ΔG should be negative which is possible only when E_{cell} is positive as n and F are always positive.

(5) Calculation of cell *emf*:

$$\text{The cell } emf, E_{cell} = E_{cathode} - E_{anode}$$

$$\text{The standard } emf, E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

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Electrochemical Series:

The arrangement of elements in the increasing order of their standard electrode potential is referred to as electrochemical series.

Electrochemical Series					
Mⁿ⁺/M	E^o volts at 298K	Mⁿ⁺/M	E^o volts at 298K	Mⁿ⁺/M	E^o volts at 298K
Li ⁺ /Li	-3.05	Al ³⁺ /Al	-1.66	H ⁺ /H	0.00
K ⁺ /K	-2.93	Zn ²⁺ /Zn	-0.76	Cu ²⁺ /Cu	0.34
Ba ²⁺ /Ba	-2.90	Fe ²⁺ /Fe	-0.44	Ag ⁺ /Ag	0.80
Ca ²⁺ /Ca	-2.87	Cd ²⁺ /Cd	-0.40	Hg ²⁺ /Hg	0.85
Na ⁺ /Na	-2.71	Sn ²⁺ /Sn	-0.14	Pt ²⁺ /Pt	1.20
Mg ²⁺ /Mg	-2.37	Pb ²⁺ /Pb	-0.13	Au ³⁺ /Au	1.38

- A negative value indicates oxidation tendency and a positive value indicates the reduction tendency with respect to hydrogen.
- The metals with lower electrode potential values are more reactive and as the electrode potential increases, the reactivity decreases and metals with higher electrode potentials are nobler.
- Metals with lower electrode potentials have the tendency to replace metals with higher electrode potential from their solutions.
For example, Zn displaces Cu and Cu displaces Ag.
- Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

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Numerical Problems on E, E⁰cell and E_{cell}

- 1) The standard electrode potential of Cd electrode is -0.40 V. If the Cd electrode is dipped in 0.025 M CdSO_4 solution at 25°C , what is the potential developed?

Given:

$$E^{\circ}_{\text{Cd}} = -0.40 \text{ V};$$

$$[\text{Cd}^{2+}] = 0.025 \text{ M at } 25^{\circ}\text{C}$$

$$n = 2$$

Solution:

- **Electrode Potential of Cd electrode:**

$$E_{\text{Cd}} = E^{\circ}_{\text{Cd}} + \frac{0.0591}{n} \log[\text{Cd}^{2+}] \text{ volts}$$

$$E_{\text{Cd}} = -0.40 + \frac{0.0591}{2} \log(0.025) \text{ volts}$$

∴ $E_{\text{Cd}} = -0.447 \text{ volts}$

- 2) Calculate the electrode potential value of a copper electrode dipped in a 0.1 M solution of CuSO_4 solution at 298K assuming CuSO_4 to be completely dissociated. The standard electrode potential of Cu^{2+}/Cu system is 0.34V at 298K .

Given:

$$E^{\circ}_{\text{Cu}} = 0.34 \text{ V};$$

$$[\text{Cu}^{2+}] = 0.1 \text{ M at } 298\text{K}$$

$$n = 2$$

Solution:

- **Electrode Potential of Cu electrode:**

$$E_{\text{Cu}} = E^{\circ}_{\text{Cu}} + \frac{0.0591}{n} \log[\text{Cu}^{2+}] \text{ volts}$$

$$E_{\text{Cu}} = 0.34 + \frac{0.0591}{2} \log(0.1) \text{ volts}$$

∴ $E_{\text{Cu}} = 0.31045 \text{ volts}$

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- 3) The *emf* of a cell $Mg/Mg^{2+} (0.01) \parallel Cu^{2+}/Cu$ is measured to be 2.78V at 298K. The standard electrode potential of Mg electrode is $-2.37V$. Calculate the electrode potential of copper electrode.

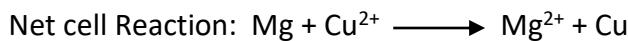
Given:



$$E_{cell} = 2.78V \text{ at } 298K$$

$$[Mg^{2+}] = 0.01M \text{ and } E^o_{Mg} = -2.37 V$$

Solution:



- **Electrode Potential of Mg electrode:**

$$E_{Mg} = E^o_{Mg} + \frac{0.0591}{n} \log[Mg^{2+}] \text{ volts}$$

$$E_{Mg} = -2.37 + \frac{0.0591}{2} \log(0.01) \text{ volts}$$

$$\textcolor{blue}{\oplus} \quad E_{Mg} = -2.4291 V$$

- **Electrode Potential of Cu electrode:**

$$E_{cell} = E_{cathode} - E_{anode} = E_{Cu} - E_{Mg}$$

$$E_{Cu} = E_{cell} + E_{Mg}$$

$$E_{Cu} = 2.78 + (-2.4291) \text{ volts}$$

$$\textcolor{blue}{\oplus} \quad E_{Cu} = 0.3509 V$$

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- 4) Write the half cell and net cell reactions for the following cell: $\text{Zn}/\text{ZnSO}_4(\text{aq}) \parallel \text{CuSO}_4(\text{aq})/\text{Cu}$. Calculate the standard emf of the cell. Given: $E^\circ_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}$ and $E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.34 \text{ V}$.

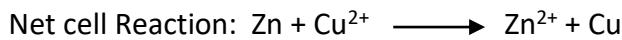
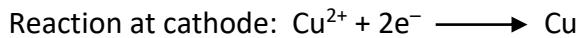
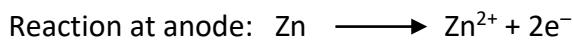
Given:



$$E^\circ_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}$$

$$E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.34 \text{ V.}$$

Solution:



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

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}} - E^\circ_{\text{Zn}}$$

$$E^\circ_{\text{cell}} = 0.34 - (-0.76)$$

➊ **$E^\circ_{\text{cell}} = 1.1 \text{ V}$**

- 5) The E° values of Li^+/Li , Zn^{++}/Zn , Cu^{++}/Cu , and Ag^+/Ag are -3.05 V , -0.76 V , $+0.34 \text{ V}$ and $+0.80 \text{ V}$ respectively. Which combination of the electrodes you use to construct a cell of highest *emf* if the ionic concentrations are 0.1 M , 1.0 M , 10 M and 0.01 M in the same order. Justify your answer.

Given:

$$E^\circ_{\text{Li}} = -3.05 \text{ V}; [\text{Li}^+] = 0.1 \text{ M}$$

$$E^\circ_{\text{Zn}} = -0.76 \text{ V}; [\text{Zn}^{2+}] = 1.0 \text{ M}$$

$$E^\circ_{\text{Cu}} = +0.34 \text{ V}; [\text{Cu}^{2+}] = 10 \text{ M}$$

$$E^\circ_{\text{Ag}} = +0.80 \text{ V}; [\text{Ag}^+] = 0.01 \text{ M}$$

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Solution:

- **Electrode Potential of Li electrode:**

$$E_{Li} = E^o_{Li} + \frac{0.0591}{n} \log [Li^+] \text{ volts}$$

$$E_{Li} = -3.05 + \frac{0.0591}{1} \log(0.1) \text{ volts}$$

➡ **$E_{Li} = -3.1091 \text{ V}$**

- **Electrode Potential of Zn electrode:**

$$E_{Zn} = E^o_{Zn} + \frac{0.0591}{n} \log [Zn^{2+}] \text{ volts}$$

$$E_{Zn} = -0.76 + \frac{0.0591}{2} \log(1.0) \text{ volts}$$

➡ **$E_{Zn} = -0.76 \text{ V}$**

- **Electrode Potential of Cu electrode:**

$$E_{Cu} = E^o_{Cu} + \frac{0.0591}{n} \log [Cu^{2+}] \text{ volts}$$

$$E_{Cu} = 0.34 + \frac{0.0591}{2} \log(10) \text{ volts}$$

➡ **$E_{Cu} = 0.3696 \text{ V}$**

- **Electrode Potential of Ag electrode:**

$$E_{Ag} = E^o_{Ag} + \frac{0.0591}{n} \log [Ag^+] \text{ volts}$$

$$E_{Ag} = 0.80 + \frac{0.0591}{1} \log(0.01) \text{ volts}$$

➡ **$E_{Ag} = 0.6818 \text{ V}$**

Since the electrode potential value of lithium is lower and that of silver is higher, the Li-Ag cell combination will form the cell with highest emf.

$$E_{cell} = E_{cathode} - E_{anode} = E_{Ag} - E_{Li} = 0.6818 - (-3.1091)$$

➡ **$E_{cell} = 3.7909 \text{ V}$**

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- 6) Calculate the potential of Zn-Ag cell at 298K if the concentration of Zn^{2+} and Ag^+ are $1.3 \times 10^{-3} M$ and $5.2 \times 10^{-6} M$ respectively. E^0 value of the cell at 298K is 1.5V. Calculate the change in free energy ΔG for the reduction of one mole of Ag^+ .

Given: 1 Faraday = 96.5 kJ/V mole.

Given:

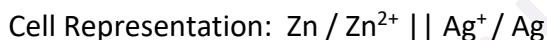
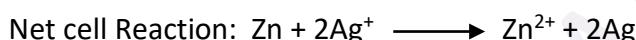
$$[Zn^{2+}] = 1.3 \times 10^{-3} M$$

$$[Ag^+] = 5.2 \times 10^{-6} M$$

$$E^0_{cell} = 1.5 V \text{ at } 298K$$

$$1 \text{ Faraday} = 96.5 \text{ kJ/V mole}$$

Solution:



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

$$E_{cell} = 1.5 - \frac{0.0591}{2} \log \frac{[1.3 \times 10^{-3}]}{[5.2 \times 10^{-6}]^2} \text{ volts}$$

$$E_{cell} = 1.5 - 0.227 \text{ volts}$$

∴ $E_{cell} = 1.2729 \text{ volts}$

- **Change in free energy ΔG for the reduction of one mole of Ag^+ :**

$$\Delta G = -nFE$$

$$n = 1 \text{ for } Ag.$$

$$\Delta G = -1 \times 96.5 \times 1.2729 \text{ kJ/mole}$$

∴ $\Delta G = -122.83 \text{ kJ/mole}$

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- 7) An electrochemical cell consists of Mg electrode dipped in 0.05M $Mg(NO_3)_2$ solution and Ag electrode dipped in 0.4M $AgNO_3$ solution. The standard electrode potentials of Mg and Ag electrodes are -2.37V and 0.80V respectively. Represent the cell, write the cell reactions and calculate the *emf* of the cell.

Given:

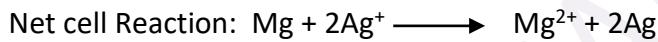
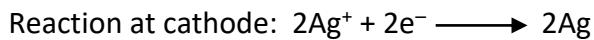
$$[Mg^{2+}] = 0.05 \text{ M}$$

$$[Ag^+] = 0.4 \text{ M}$$

$$E^\circ_{Mg} = -2.37 \text{ V}$$

$$E^\circ_{Ag} = 0.80 \text{ V}$$

Solution:



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

$$E^\circ_{cell} = E^\circ_{Ag} - E^\circ_{Mg}$$

$$E^\circ_{cell} = 0.80 - (-2.37) \text{ V}$$

■ $E^\circ_{cell} = 3.17 \text{ V}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Mg^{2+}]}{[Ag^+]^2} \text{ volts}$$

$$E_{cell} = 3.17 - \frac{0.0591}{2} \log \frac{[0.05]}{[0.4]^2} \text{ volts}$$

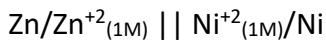
■ $E_{cell} = 3.1849 \text{ volts}$

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- 8) If the emf of $Zn/Zn^{+2}_{(1M)}$ || $Ni^{+2}_{(1M)}/Ni$ is 0.51 V and $Ni/Ni^{+2}_{(1M)}$ || SCE is 0.49 V, then calculate $E^o_{Zn^{+2}/Zn}$. Given: $E^o_{SCE} = 0.24V$.

Given:



$$E_{cell} = 0.51 \text{ V}$$



$$E_{cell} = 0.49 \text{ V}$$

$$E^o_{SCE} = 0.24 \text{ V}$$

Solution:

Consider $Ni/Ni^{+2}_{(1M)} \parallel SCE$ cell

Since $[Ni^{2+}] = 1\text{M}$ and standard calomel electrode is used, the $E_{cell} = E^o_{cell} = 0.49 \text{ V}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = E^o_{SCE} - E^o_{Ni}$$

$$E^o_{Ni} = E^o_{SCE} - E^o_{cell}$$

$$E^o_{Ni} = 0.24 - 0.49 \text{ V}$$

$$\text{Ans} \quad E^o_{Ni} = -0.25 \text{ V}$$

Consider $Zn/Zn^{+2}_{(1M)} \parallel Ni^{+2}_{(1M)}/Ni$

Since $[Zn^{2+}] = 1\text{M}$ and $[Ni^{2+}] = 1\text{M}$, the $E_{cell} = E^o_{cell} = 0.51 \text{ V}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = E^o_{Ni} - E^o_{Zn}$$

$$E^o_{Zn} = E^o_{Ni} - E^o_{cell}$$

$$E^o_{Ni} = -0.25 - 0.51 \text{ V}$$

$$\text{Ans} \quad E^o_{Ni} = -0.76 \text{ V}$$

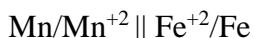
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- 9) Calculate the voltage in the following cell $\text{Mn}/\text{Mn}^{+2} \parallel \text{Fe}^{+2}/\text{Fe}$, when Fe rod is immersed in 1M FeSO_4 solution and Mn rod is immersed in 0.1M MnSO_4 solution.

Given: $E^{\circ}_{\text{Mn}^{+2}/\text{Mn}} = -1.18\text{V}$ and $E^{\circ}_{\text{Fe}^{+2}/\text{Fe}} = -0.44\text{V}$ and

Given:



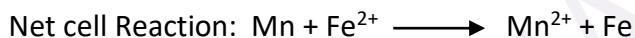
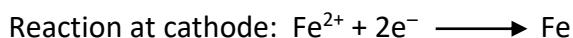
$$E^{\circ}_{\text{Fe}^{+2}/\text{Fe}} = -0.44 \text{ V}; [\text{Fe}^{2+}] = 1 \text{ M}$$

$$E^{\circ}_{\text{Mn}^{+2}/\text{Mn}} = -1.18\text{V}; [\text{Mn}^{2+}] = 0.1 \text{ M}$$

Solution:

$$E^{\circ}_{\text{Mn}^{+2}/\text{Mn}} < E^{\circ}_{\text{Fe}^{+2}/\text{Fe}}$$

Hence, Mn acts as anode and Fe acts as cathode



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

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Fe}} - E^{\circ}_{\text{Mn}}$$

$$E^{\circ}_{\text{cell}} = -0.44 - (-1.18) \text{ V}$$

$$\text{E}^{\circ}_{\text{cell}} = 0.74 \text{ V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Mn}^{2+}]}{[\text{Fe}^{2+}]} \text{ volts}$$

$$E_{\text{cell}} = 0.74 - \frac{0.0591}{2} \log \frac{[0.1]}{[1]} \text{ volts}$$

$$\text{E}_{\text{cell}} = 0.76955 \text{ volts}$$

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- 10) A cell is formed by dipping Ni rod in 0.01M Ni^{2+} solution and Pb rod in 0.5M Pb^{2+} solution. The standard electrode potentials of Nickel and Lead are -0.24 V and -0.13 V respectively. Write the cell representation, cell reactions and calculate EMF of the cell.

Given:

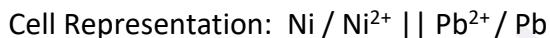
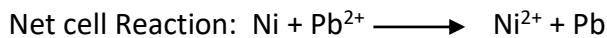
$$E^{\circ}_{\text{Ni}} = -0.24 \text{ V}; [\text{Ni}^{2+}] = 0.01 \text{ M}$$

$$E^{\circ}_{\text{Pb}} = -0.13 \text{ V}; [\text{Pb}^{2+}] = 0.5 \text{ M}$$

Solution:

$$E^{\circ}_{\text{Ni}} < E^{\circ}_{\text{Pb}}$$

Hence, Ni acts as anode and Pb acts as cathode



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

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

$$E^{\circ}_{\text{cell}} = -0.13 - (-0.24) \text{ V}$$

⊕ **$E^{\circ}_{\text{cell}} = 0.11 \text{ V}$**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Pb}^{2+}]} \text{ volts}$$

$$E_{\text{cell}} = 0.11 - \frac{0.0591}{2} \log \frac{[0.01]}{[0.5]} \text{ volts}$$

⊕ **$E_{\text{cell}} = 0.1602 \text{ volts}$**

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BATTERIES

Battery is a device consisting of two or more galvanic cells connected in series or parallel or both, that can store chemical energy in the form of active materials and on demand convert into electrical energy through electrochemical redox reaction to drive an external circuit. Batteries can thus generate power and can act as a portable source of electrical energy.

Battery technology has acquired greater importance in recent times since the petroleum resources of the world are fast depleting resulting in greater dependency on alternative energy sources.

The major driving forces for battery technology were the revolution in micro-electronics and increased demand for portable gadgets powered by batteries. The size of the modern dry batteries ranges from a fraction of a cubic centimeter to several cubic decimeters.

Applications:

Batteries are used in calculators, watches, pacemakers for heart, hearing aids, computers, car engines, stand-by power supplies, emergency lighting in hospitals, electroplating industrial tractions, military and in 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 concept

The basic electrochemical unit in a battery is a galvanic cell.

Principal Components of Battery:

The battery consists of four major components.

- **The anode (negative electrode):** It gives out electrons to the external circuit by undergoing oxidation during electrochemical reaction.

The anode selected should contain following properties: Easy oxidation; delivery of high columbic output; good conductivity; good stability; ease of fabrication and low cost.

Zinc is predominantly used as anode since it has the properties mentioned above. Lithium, the lightest metal is being widely used as an anode in the modern batteries.

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- **The Cathode (positive electrode):** It accepts electrons from the external circuit and reduction of an active species occurs.
The cathode should facilitate the reduction of active species in the medium; It must be stable when in contact with the electrolyte and have a useful working voltage.
- **The Electrolyte (ionic conductor):** The electrolyte is commonly a solution of acids, alkalis or salts having high ionic conductivity. Solid electrolytes with appreciable ionic conductivities are also used at the operating temperature of the cell.
The electrolyte must have good ionic conductivity but poor electrical conductivity to prevent internal short circuiting. Electrolyte should be non-reactive with the electrode materials. It should be safe to handle.
- **The Separator:** The material which electronically isolates anodes and cathodes in a battery to prevent internal short circuiting are called separators. They are permeable to the electrolyte so as to maintain desired ionic conductivity.
The separator should permit ions to pass easily from anode to cathode compartment and vice versa both during discharging and charging.
Materials used most commonly as separators include fibrous forms of regenerated cellulose, vinyl polymers, polyolefin, cellophane and nafion membranes.

Note:

Containers used for battery construction must be resistance to corrosion from both inside and outside the cell.

Operation of a battery during discharge and charge process

During discharge:

The Battery acts as voltaic cell. That is oxidation takes place at anode (negative electrode) and reduction of active species takes place at cathode (positive electrode).

During charging:

The battery acts as an electrolytic cell. The current flow is reversed and oxidation takes place at anode (positive electrode) and reduction of active species takes place at cathode (negative electrode).

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LITHIUM BATTERIES

Selection of Lithium as an anode material:

Lithium is a theoretically active material for negative electrode of the electrochemical cells owing to its least noble nature and low specific gravity.

Lithium metal offers an attractive option to be used as a battery anode material because of its light weight, low electrode potential, high electrochemical equivalence and good conductivity.

Because of these outstanding features, the use of lithium has predominated in the development of high performance primary and secondary batteries.

Selection of Electrolyte for Lithium batteries:

The electrolyte used in lithium batteries cannot be aqueous solutions because of high reactivity of lithium with water. Therefore non-aqueous electrolytes are to be used in lithium batteries.

Advantages of Lithium batteries

- High cell voltage.
- High energy density due to low atomic mass of lithium.
- Good power density.
- Operation over a wide range of temperature from about -40°C to 70°C.
- Flat discharge voltage characteristics.
- Superior shelf life.

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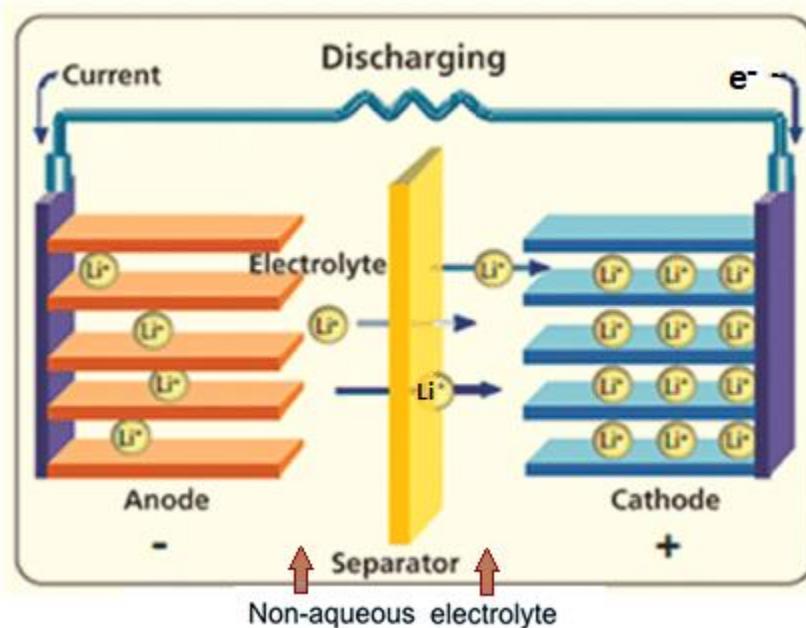
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Li - ION BATTERY

The most commercially used secondary battery is the Li – ion battery.

CONSTRUCTION:

- The Li – ion battery (LIBs) uses **lithiated graphite**, LiC_6 (maximum capacity of 372mAh/g) as an **anode** and a layered oxide such as **lithium cobalt(III)oxide**, LiCoO_2 as a **cathode** material.
- Lithiated graphite, LiC_6 has a layered structure that can support and store the small lithium ions in between its layers.
- Lithiated graphite, like pure lithium, reacts vigorously with water to form lithium hydroxide (Li-OH) and hydrogen gas. Thus, a non-aqueous electrolyte is typically used.
- The organic solvent such as **ethylene carbonate** containing complexes of lithium ions, **lithium hexafluorophosphate**, LiPF_6 is used as a non-aqueous electrolyte.
- The non-woven micro porous polypropylene film impregnated with the non-aqueous electrolyte is used as a separator and is placed in between the anode and cathode.
- A sealed container rigidly excludes moisture from the battery pack is typically used.



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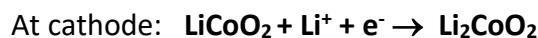
Cell Reaction:

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.

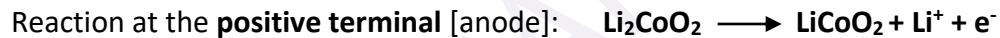
The lithium ions are transported to and fro from the anode or cathode, by reducing the transition metal, cobalt in LiCoO_2 from Co^{3+} to Co^{2+} during discharge and by oxidizing the transition metal, cobalt in Li_2CoO_2 from Co^{2+} to Co^{3+} during charge.

WORKING:

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



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



Voltage:

The cell potential is around 4.2 volts.

Advantages:

Higher energy density; higher voltage; flat discharge voltage.

Applications:

Lithium-ion battery is used for cell phones, laptops, cameras, consumer electronic devices and in safety and security devices.

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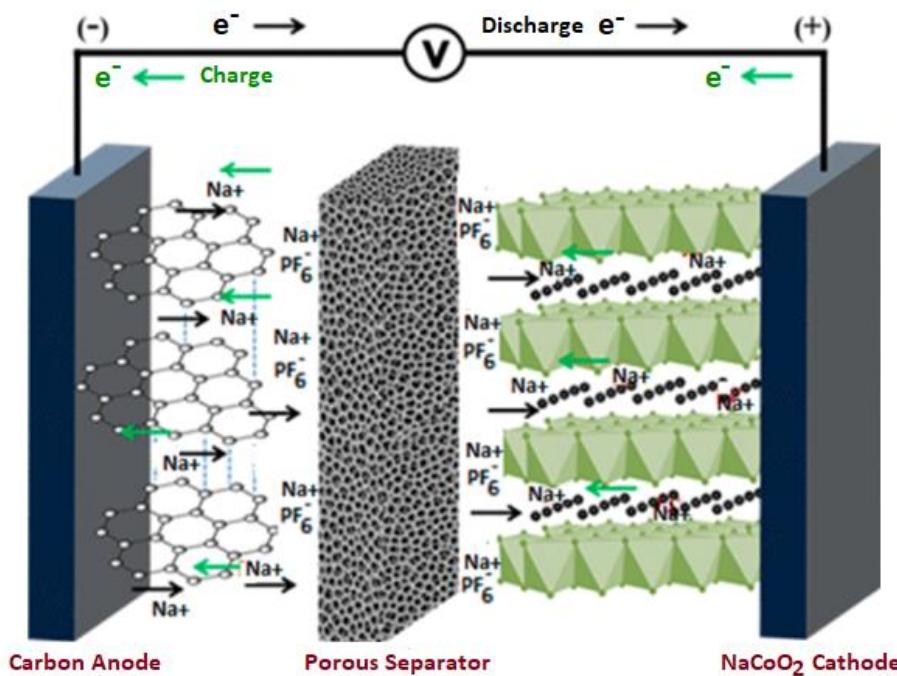
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Na - ION BATTERY

Sodium-ion batteries (NIBs) are rechargeable batteries that use sodium ions to carry a charge. They're similar to lithium-ion batteries in that they're both alkaline and have a similar operating principle, but sodium-ion batteries replace lithium with sodium as the charge carrier.

CONSTRUCTION:

- **Anode:** Typically made of hard carbon, graphite, or other materials such as **NaC₆** that can reversibly store and release sodium ions.
- **Cathode:** Usually cathode is composed of layered oxide materials such as **sodium cobalt(III)oxide, NaCoO₂** which can accommodate sodium ions.
- **Electrolyte:** The organic solvent such as **ethylene carbonate** containing complexes of sodium ions, **sodium hexafluorophosphate, NaPF₆** is used as an electrolyte.
- **Separator:** A non-woven micro porous polypropylene film impregnated with the non-aqueous electrolyte is used as a separator and is placed in between the anode and cathode.
- **Container:** A sealed container rigidly excludes moisture from the battery pack is typically used.



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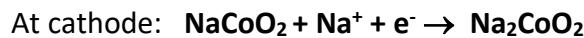
Cell Reactions:

In sodium-ion battery, sodium 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 sodium ions make the reverse journey during charging.

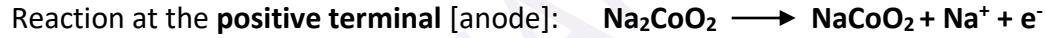
The sodium ions are transported to and fro from the anode or cathode, by reducing the transition metal, cobalt in NaCoO_2 from Co^{3+} to Co^{2+} during discharge and by oxidizing the transition metal, cobalt in Na_2CoO_2 from Co^{2+} to Co^{3+} during charge.

WORKING:

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



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



Voltage:

The cell potential is around 4.3 volts.

Advantages:

- **Abundant materials:** Sodium is plentiful and readily available, unlike lithium, reducing reliance on scarce resources.
- **Lower cost:** Sodium materials are generally cheaper than lithium-based ones, potentially leading to more affordable batteries.
- **Safety:** NIBs generally exhibit better thermal stability and lower flammability compared to lithium-ion batteries.
- **Environmental benefits:** Lower extraction and processing impact compared to lithium mining.

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Applications:

- Grid storage: Stationary energy storage for renewable energy sources like solar and wind.
- Electric vehicles: NIBs with improved performance could offer a cost-effective alternative for shorter-range EVs.
- Industrial applications: Backup power for various industrial equipment and processes.
- Consumer electronics: Potential use in portable electronics like wireless ear-buds and smart watches, but performance needs improvement.

Challenges:

- Lower energy density: NIBs typically have lower energy density compared to lithium-ion batteries, limiting their application range.
- Slower charging/discharging: NIBs often exhibit slower charging and discharging rates, impacting some applications.
- Electrode materials: Development of high-performance and affordable anode and cathode materials is crucial for wider adoption.

Future Outlook:

- With continuous research and development efforts, sodium-ion batteries have the potential to become a significant player in the sustainable energy landscape.
- Addressing the challenges related to energy density, performance, and cost will unlock their full potential in various applications, contributing to a more sustainable future.
- Different types of NIBs are under development, each with its own advantages and limitations.
- Recycling infrastructure for NIBs is still emerging, requiring further efforts for responsible end-of-life management.
- Collaboration between academic and industrial researchers is crucial for accelerating the development and commercialization of sodium-ion batteries.

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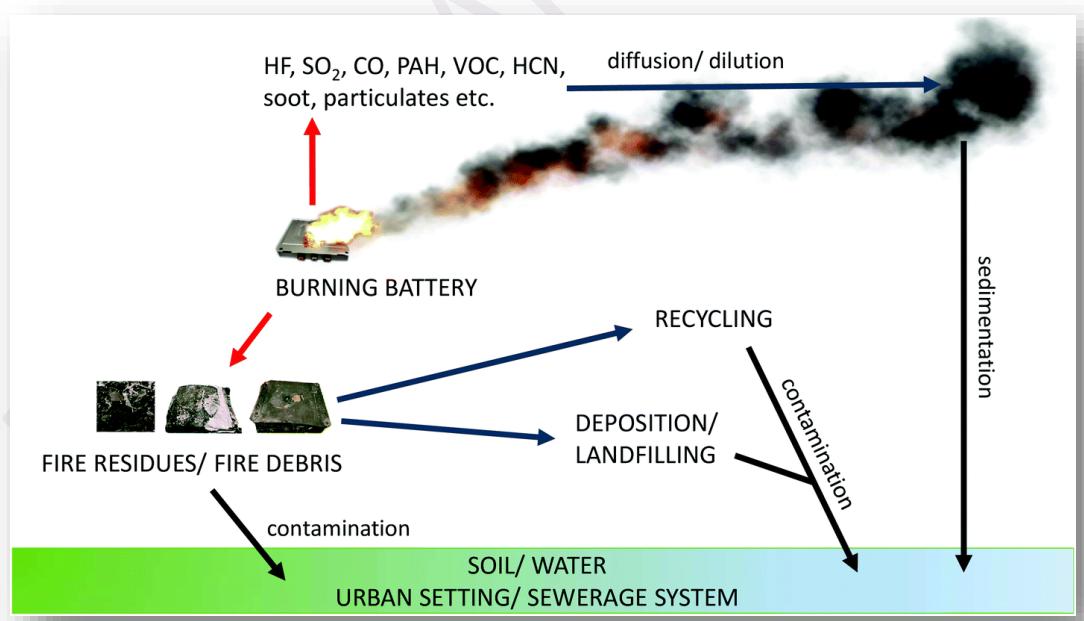
Sustainable Recycling of Batteries

Introduction:

Batteries play a pivotal role in powering our modern world, from portable electronics to electric vehicles. However, the disposal of batteries poses significant environmental challenges due to the presence of toxic materials such as lead, cadmium, and mercury. Sustainable recycling of batteries is crucial to mitigate environmental pollution, conserve resources, and minimize health hazards associated with improper disposal. This course material will delve into the disposal problems of batteries, the health hazards they pose to the environment, methods of recycling batteries, their outcomes, and the future scope of sustainable battery recycling.

Disposal Problems:

The improper disposal of batteries presents numerous environmental challenges. When batteries end up in landfills, they release toxic metals and chemicals into the soil and groundwater, contaminating ecosystems and posing risks to human health. Furthermore, incinerating batteries can release harmful pollutants into the air, contributing to air pollution and climate change. The increasing proliferation of batteries exacerbates these disposal problems, necessitating sustainable recycling solutions.



(adapted from ISO, 2011; Stec *et al.*, 2019).

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Health Hazards of Battery Disposal:

The disposal of batteries in the environment poses significant health hazards. Lead-acid batteries, commonly used in vehicles and industrial applications, contain lead, a potent neurotoxin that can cause neurological damage, especially in children. Similarly, cadmium and mercury found in rechargeable batteries can accumulate in the environment and bioaccumulation in the food chain, posing risks to human health and ecosystem integrity. Inhalation of battery fumes or ingestion of contaminated water or food can lead to acute or chronic health effects, including respiratory problems, kidney damage, and developmental disorders.

Dangers of Throwing Away Lithium-Ion Batteries



Li-ion batteries leak **environmental contaminants** like cobalt, manganese, nickel, and lithium salts.



Damaged lithium-ion batteries may **release harmful particles** with the aerodynamic diameters of less than 10 or 2.5 µm.



If a charged lithium cell is crushed or pierced, it will short-circuit which also causes thermal runoff that leads to **combustion or explosion**.



Lithium-ion leachates can transport hazardous chemicals and organisms **contaminating solid and groundwater** along the way.

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Methods of Recycling Batteries:

Sustainable recycling offers a solution to mitigate the environmental and health impacts of battery disposal. Several methods are employed to recycle batteries, including:

Hydrometallurgical Recycling:

This method involves leaching metals from batteries using aqueous solutions, followed by purification and recovery of metals through precipitation or solvent extraction. It is particularly suitable for recycling lead-acid batteries.

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Pyro-metallurgical Recycling:

Pyro-metallurgical processes involve melting batteries at high temperatures to separate metals from non-metallic components. The recovered metals can be used to manufacture new batteries or other products.

Mechanical Recycling:

Mechanical recycling entails shredding batteries to separate components based on size and density. This method is commonly used for recycling alkaline batteries, where metals such as zinc and manganese can be recovered for reuse.

Direct Recycling:

Direct recycling involves refurbishing spent batteries to extend their lifespan or repurposing them for secondary applications, such as energy storage in stationary systems.

Outcomes and Future Scope:

Sustainable recycling of batteries yields several positive outcomes:

Resource Conservation:

Recycling batteries conserves valuable metals and reduces the need for virgin materials extraction, thereby conserving natural resources.

Pollution Reduction:

Recycling mitigates environmental pollution by preventing the release of toxic metals and chemicals into the environment.

Economic Opportunities:

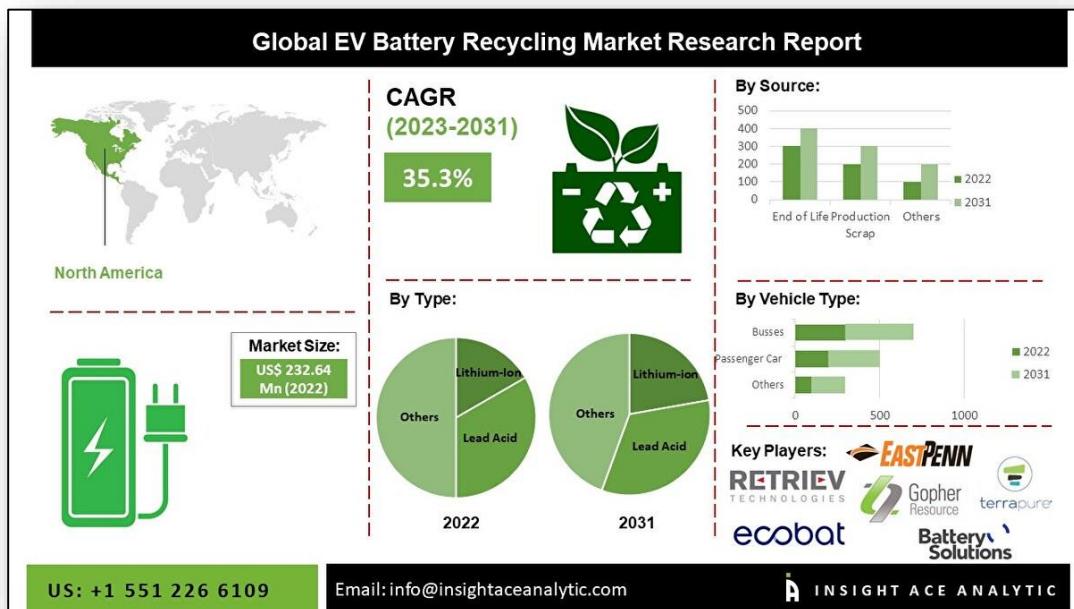
Recycling facilities create jobs and contribute to the circular economy by recovering valuable materials from spent batteries.

Regulatory Compliance:

Compliance with regulations on battery disposal and recycling ensures environmental protection and public health.

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The future scope of sustainable battery recycling involves technological advancements to improve recycling efficiency, develop novel recycling processes, and promote circular economy principles. Additionally, public awareness and education campaigns can encourage responsible battery disposal and promote recycling initiatives at the community level.

In conclusion, sustainable recycling of batteries is essential to address the environmental and health hazards associated with battery disposal. By employing various recycling methods and embracing technological innovations, we can achieve resource conservation, pollution reduction, and economic prosperity while ensuring a sustainable future for generations to come.

Sustainable Batteries: Powering a Greener Future:

The demand for reliable and efficient energy storage is growing rapidly, driven by factors like electric vehicles, renewable energy integration, and portable electronics. While conventional batteries offer solutions, their environmental impact can raise concerns. Therefore, the concept of "sustainable batteries" is gaining traction, focusing on minimizing their environmental footprint throughout their lifecycle.

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Key Characteristics of Sustainable Batteries:

Material sourcing:

Utilize abundant and responsibly sourced materials, minimizing reliance on conflict minerals and rare earth elements.

Production:

Employ low-energy and environmentally friendly manufacturing processes, reducing greenhouse gas emissions and harmful waste.

Use phase:

Offer high energy density, long lifespan, and minimal maintenance to maximize efficiency and minimize resource consumption.

End-of-life:

Enable efficient and safe recycling or repurposing of battery components, minimizing landfill waste and recovering valuable materials.

Promising Technologies for Sustainable Batteries:

Sodium-ion batteries:

Offer a more abundant and less-polluting alternative to lithium-ion batteries, but research is ongoing to improve their energy density and cycle life.

Redox flow batteries:

Store energy in liquid electrolytes, enabling flexibility in design and scalability, but require larger volumes compared to solid-state batteries.

Organic batteries:

Utilize organic materials, potentially offering safer and bio-based options, but face challenges in terms of cost and performance.

Solid-state batteries:

Use non-flammable solid electrolytes, enhancing safety and potentially offering higher energy density, but are still under development.

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Challenges and Opportunities:

Technological advancements:

Further research and development are needed to improve performance, scalability, and cost-effectiveness of sustainable battery technologies.

Standardization and regulations:

Clear standards and regulations for recycled content, battery performance, and end-of-life management are crucial for wider adoption.

Supply chain sustainability:

Responsible sourcing of materials, fair labor practices, and reduced resource extraction are essential for a truly sustainable battery ecosystem.

Impact and Future Outlook:

Sustainable batteries have the potential to revolutionize the energy landscape, enabling cleaner and more efficient solutions for various applications. By addressing the challenges, collaborating across industries and academia, and investing in research and development, we can unlock the full potential of these technologies for a sustainable future. Each type of sustainable battery technology has its own advantages and disadvantages, and the best choice depends on the specific application and sustainability goals.

- Life cycle assessments are crucial for evaluating the overall environmental impact of different battery technologies.
- Consumer awareness and demand for sustainable products can create market forces driving innovation and adoption.

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FUELS CELLS

Motor vehicles account for about $\frac{1}{2}$ of the total hydrocarbon and nitrogen oxide pollution at the global level. The hydrocarbons and oxides of nitrogen combine to form photochemical smog that pollutes the atmosphere in many towns and cities. This has led to stringent emission legislation requiring zero emission vehicles.

Use of storage batteries to power cars is one alternate option. But recharging of storage batteries requires electricity which is to be generated by burning coal during which CO_2 and SO_2 are emitted. The increase of CO_2 in atmosphere causes green house effect leading to global warming.

The large scale manufacture of storage batteries such as Ni-Cd and Lead accumulators leads to the discharge of many toxic chemicals.

An electric car equipped with a fuel cell is the only viable option to reduce pollution caused by battery operated motor cars.

Definition:

A fuel cell is a galvanic cell in which the chemical energy contained in a readily available fuel - oxidant system is converted directly into electrical energy by means of electrochemical process in which the fuel is oxidized at the anode.

A fuel cell consists of two electrodes and an electrolyte. However, the fuel and the oxidizing agents are continuously and separately supplied to the two respective electrodes of the cell, at which they undergo oxidation and reduction reactions.

These cells are capable of supplying current as long as they are supplied with the reactants.

A fuel cell may be represented as

Fuel / electrode / electrolyte / electrode / Oxidant

At the anode fuel undergoes oxidation and at the cathode oxidant undergoes reduction.



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As in any electrochemical cell, the electrical energy produced in a fuel cell corresponds to the free energy change of the electrode processes.

$$-\Delta G = nFE_{\text{cell}}$$

where ΔG is decrease in free energy change of the fuel cell reaction; n is number of electron transfer; F is Faraday and E_{cell} is the emf of fuel cell in volts.

Differences between a battery and a fuel cell:

- In a fuel cell, the reactants are fed from outside the cell and do not form an integral part as in a battery.
- Unlike batteries, fuel cells do not store chemical energy.
- Reactants are constantly supplied and the products are constantly removed from a fuel cell.

Advantages of fuel cells:

- Power efficiency of fuel cells is high.
- They are eco-friendly since the products of the overall reactions are not toxic and hence pose no pollution problems.
- They can produce direct currents for long periods at low cost.
- No moving parts and so elimination of wear and tear.
- Silent operation and low maintenance.
- No need of charging.

Disadvantages of fuel cells:

- Cost of power is high as a result of cost of electrodes.
- Fuels in the form of gases and oxygen need to be stored in tanks under high pressure.
- Power output is moderate.
- To have an appreciable voltage, a battery of fuel cells must be available.
- High price of clean hydrogen.
- Present lack of infrastructure to distribute hydrogen.

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Types of Fuel cells:

Fuel cells are generally classified on the basis of electrolyte, because the electrolyte determines the operating temperature of a system and in part the kind of fuel that can be employed.

There are five principal types of fuel cells.

- Alkaline Fuel Cell (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Polymer Electrolyte Membrane Fuel Cell (PEMFC)
- Solid Oxide Fuel Cell (SOFC)

An electrolyte and two electrodes are the essential components of all fuel cells, but the electrolyte is what differentiates them. The electrolyte is a substance that conducts ions but not electricity. It can be a **liquid** or a **solid** or a **membrane** depending on the type of the fuel cell.

- Alkaline Fuel Cell (AFC) uses liquid electrolytes like solutions of NaOH or KOH.
- Phosphoric acid fuel cells (PAFCs) utilize a concentrated 100% phosphoric acid liquid as an electrolyte.
- Molten Carbonate Fuel Cell (MCFC) uses fused carbonates (eutectic mixture of lithium carbonate and sodium or potassium carbonate) as an electrolyte.
- Polymer Electrolyte Membrane Fuel Cells (PEMFC) use a water based or mineral-acid based polymer membrane as an electrolyte.
- Solid Oxide Fuel Cells (SOFC) uses a non-porous metal oxide as an electrolyte.

As a result, the conduction mechanisms are different. SOFCs have ionic conductions accomplished by oxygen ions while PAFCs have the permeation of hydrogen ions through the electrolyte layer.

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METHANOL - OXYGEN FUEL CELL

Selection of Methanol as fuel:

Methanol is one of the most electro active organic fuels in the low temperature range. CH_3OH is used mainly as fuel because

- Methanol has low carbon content;
- It possesses a readily oxidizable $-\text{OH}$ group and
- It has high solubility in aqueous electrolytes.

Selection of Electrolyte for $\text{CH}_3\text{OH} - \text{O}_2$ fuel cell:

- The use of alkali as an electrolyte causes problems. Since the CO_2 produced during fuel cell reaction is absorbed by the electrolyte and the electrolyte is gradually converted into carbonates.



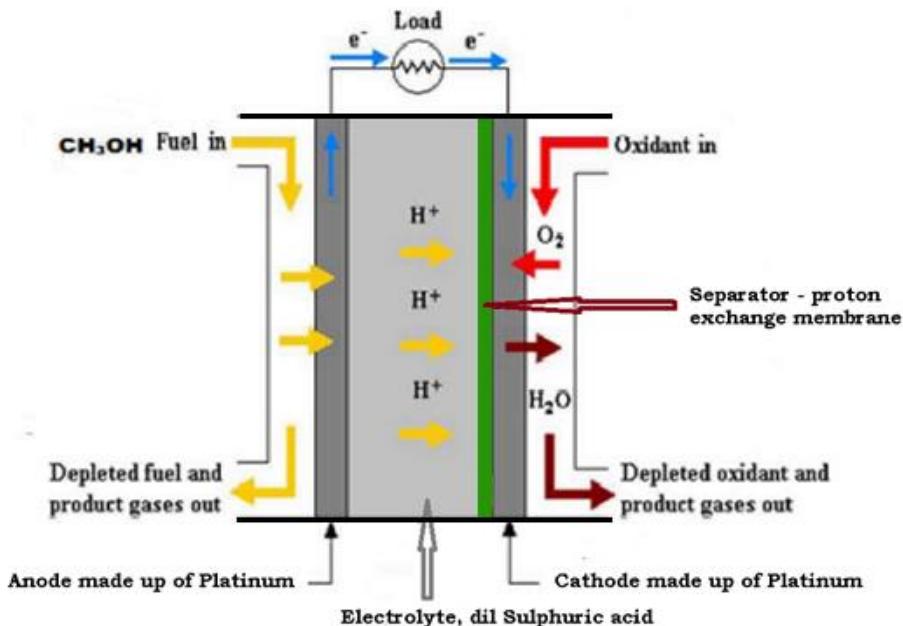
- The carbonates so formed decrease the fuel cell efficiency because of the increasing concentration polarization at the electrode surface. Further, it blocks the electrode pores and electrolyte pathways and decreases the conductivity of the electrolyte. Finally, the fuel cell becomes inoperative.
- Therefore, **acid electrolytes** are better option. An advantage of use of an acid electrolyte, dil. H_2SO_4 in place of KOH is that, CO_2 , a product of FC reaction can be removed easily.

CONSTRUCTION:

- In this fuel cell, methanol is used as fuel and oxygen is used as an oxidant.
- In $\text{CH}_3\text{OH}-\text{O}_2$ fuel cell, both the electrodes: anode and cathode are made up of Platinum.
- The electrolyte, dilute Sulphuric acid is placed in the central compartment.
- A proton exchange membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode and to reduce the presence of methanol near the cathode.
- In the absence of membrane, diffusion of the dissolved methanol through the electrolyte in the central compartment to cathode takes place and chemical oxidation of methanol occurs instead of oxidation of methanol at anode and reduction of O_2 at cathode.

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Methanol – Oxygen fuel cell

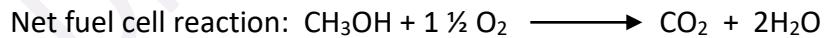
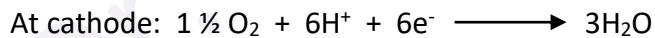
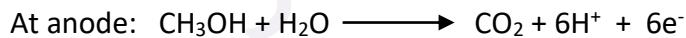
A methanol - oxygen fuel cell may be represented as:



WORKING:

Methanol and oxygen are sent continuously into their respective electrodes and electrical energy is produced with the continuous replenishment of fuel and oxidant at the respective electrodes. The *emf* of $\text{CH}_3\text{OH} - \text{O}_2$ fuel cell is 1.25V.

Electrode reactions during discharge process:



APPLICATIONS:

- Methanol – oxygen fuel cell is used in military applications.
- It is used in large scale power production.