Chapter-IV
Energy Conservation & Storage

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Syllabus of Engineering Chemistry (Theory)

Module No	Module Description	Hrs.
4	**Energy conversion and storage:** Fuel cells – Electrochemistry of a H_2–O_2 fuel cell, Basics of solid oxide fuel cells-applications; Limitations of Batteries. **Batteries- Chemical change and Electrical Work**; Electrochemical reactions; Primary cells: Lechlanche, alkaline and Li-primary cells. Secondary cells - Lead – acid, Ni-Cd, Ni-MH cells; Rechargeable lithium cells – $LiCoO_2$ and LiC_6 chemistry and applications.	8

Text Books / Reference Books

1) O. G. Palanna, Engineering Chemistry, Tata McGraw Hill Education

2) Jain P. C. and Monica Jain, Engineering Chemistry, Dhanpat Rai Publishing Company Ltd.

3) R. L. Madan, Physical Chemistry, McGraw Hill Education

4) Dara S. S., Umare S. S., Engineering Chemistry, S. Chand & Company Ltd.

5) Shashi Chawala, Chemistry, Dhanpat Rai & Co. New Delhi

Battery

Electrochemical Cell is a device which converts chemical energy into electrical energy and vice versa.

A Cell or battery is a source of electrical energy and has two electrodes (or half cells) that generates electrical energy. The EMF generated depends upon the magnitude of the electrode potentials of two electrodes.

Battery is the arrangement of two or more galvanic cells connected in series. **The working principal of battery is the transformation of free energy change of redox reaction of electrode into electrical energy.**

Characteristic of a Battery

- **Free Energy Change:** Whenever reaction takes place in a battery then the Gibb's Free Energy of redox system decreases. i.e. $\Delta G = - nFE$
- **EMF of the Battery:** The EMF of the battery depends on the total number of cells which constitute a battery.

$$M_1 + M_2^{n+} \longrightarrow M_1^{n+} + M_2$$

$$E = E^o_{cell} - \frac{0.0591}{n} \log_{10} (M_1^{n+}/M_2^{n+})$$

The EMF of the battery increases with the increase in the potential difference between the electrodes and decreases with the increase in concentration of M_1^{n+}

- **Ampere-Hour:** Rate at which electron flows in wire. The unit is coulombs/sec. An electron has a charge of 1.602×10^{-19} coulombs & an ampere is 6.24×10^{-18} electrons/sec

- **Capacity:** The capacity of battery is the total quantity of electricity involved in the electrochemical reaction or total number of Ampere hour or Watt hour can be withdrawn from a fully charged cell or battery.

$$Q = xnF$$

x = No. of moles of reaction
n = No. of electrons transferred/mole of reaction
F = Faraday's Constant = 96500 columbs

- **Power:** The power generated by a battery can be calculated as $W = V*I$

V = Cell Voltage
I = Cell Current

- **Power Density:** Power density is the ratio power delivery by a cell or battery to its weight.

Power Density = Power / Mass

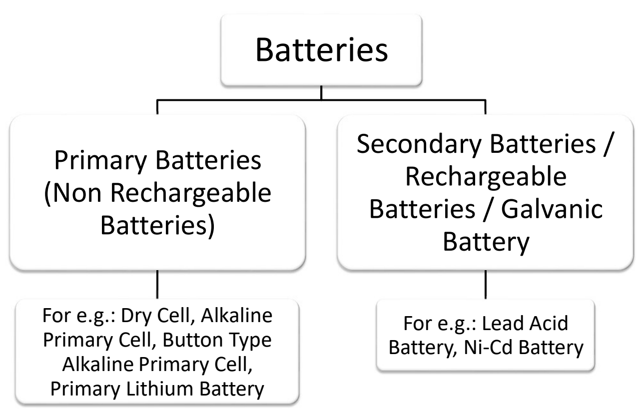
During discharging the power density decreases.

- **Energy Density:** Energy density is the ratio of amount of charge that can be stored or the energy output of a battery to its weight.

Energy Density = Watt Hour / Mass

- **Efficiency:** Ratio of output of the battery on discharge to the input required to restore it to initial state of the charge under specified condition.
- **Shelf Life:** The duration of storage at the end of which a cell or battery still retains the ability to give a specified performance.

Classification of Batteries



Primary Battery

The working principal of a primary cell is the conversion of the free energy change of the redox system into electrical energy. The net cell reaction is irreversible & they can not be recharged or used again.

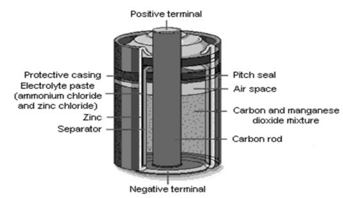
Example: Dry Cell (Leclanche Cell), Alkaline Primary Cell [Mercury Cell or Reuben Mallori (RM) Cell], Button Type Alkaline Primary Cell

Primary Battery or Dry Cell or Leclanche Cell

Zn-MnO_2 (Dry Cell)

$Zn/Zn^{2+}//NH_4^+/MnO_2/C$

Anode- Zn Cylinder
Cathode- MnO_2/Carbon
Electrolyte-$ZnCl_2$+NH_4Cl



In this cell, anode consist of Zinc container while cathode is graphite rod surrounded by powdered Magnese Dioxide (MnO_2) and Carbon.

The space between the electrodes is filled with the paste of NH_4Cl and $ZnCl_2$ & whole assembly is wrapped with polypropylene or cardboard to prevent leakage.

Anodic Reaction
$Zn \longrightarrow Zn^{2+} + 2e^-$
Cathodic Reaction
$2\ MnO_2 + 2\ H_2O + 2e^- \longrightarrow 2\ MnO(OH) + 2\ OH^-$
Net Cell Reaction
$Zn + 2\ MnO_2 + 2\ H_2O \longrightarrow 2\ MnO(OH) + Zn^{2+} + 2\ OH^-$

Secondary reaction also takes place inside the cell but do not contribute to the EMF of the cell
$2NH_4Cl + 2OH^- \longrightarrow 2NH_3 + 2\ H_2O + Cl^-$
$Zn^{2+} + 2NH_3 + 2\ Cl^- \longrightarrow Zn(NH_3)_2Cl_2$

Dry Cell do not have long life as NH_4Cl which is acidic, corrode the zinc container even if the cell is not in use. The Cell potential of dry cell lies in the range 1.25 V to 1.5 V.

Alkaline Primary Cell/ Battery or Reuben-Mallori Cell

The NH_4Cl used in dry cell is acidic and corrode the zinc container so it has limited shelf life. In order to overcome this problem alkaline KOH is used to obtain better shelf life.

There are two types of alkaline primary cell:
1) HgO-Zn Cell
2) Ag_2O-Zn Cell

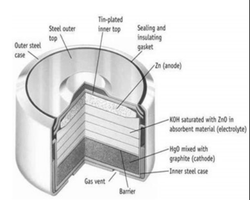
HgO-Zn Cell

It is also known as Reuben-Mallori Cell.

In this cell amalgamated Zinc rod is at the centre which act as anode of the cell. An absorbent material (cellulose) containing 40% of KOH saturated with ZnO surrounds anode.

Anode is surrounded with a paste of 5-10% graphite in HgO which is introduced in a steel case which act as cathode. Anode and cathode are separated by a layer of insulating material.

Anodic Reaction
$Zn + 2\ OH^- \longrightarrow ZnO\ (s) + H_2O + 2e^-$
Cathodic Reaction
$HgO + H_2O + 2e^- \longrightarrow 2\ Hg(s) + 2\ OH^-$
Net Cell Reaction
$Zn + HgO \longrightarrow ZnO\ (s) + Hg\ (s)$



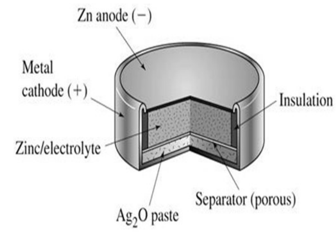
The volatage of RM cell is 1.35V. It has high capacity and the potential remains constant till its shelf life.

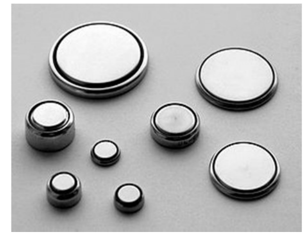
Used in electronics watches, electronic gadgets etc.

Ag_2O-Zn Cell

Alkaline Primary Cell Battery is commonly known as Button Type alkaline primary cell.

In this cell Ag_2O is pressed into thin button type metal case which act as cathode. Zinc metal is at the centre of the cell & behaves as Anode. An absorbent material soaked in KOH is placed between cathodic and anodic compartments. Electrolyte is KOH solution.





Anodic Reaction
$Zn + 2\,OH^- \longrightarrow ZnO\,(s) + H_2O + 2e^-$
Cathodic Reaction
$Ag_2O + H_2O + 2e^- \longrightarrow 2\,Ag + 2\,OH^-$
Net Cell Reaction
$Zn + Ag_2O + 2\,H_2O \longrightarrow ZnO\,(s) + 2\,Ag\,(s)$

The Cell potential of dry cell lies in the range 1.25 V to 1.5 V.

The alkaline battery has better performance due to high voltage, longer life, more reliability and non-toxicity.

They are used in calculators, electronic watches etc.

Secondary Battery

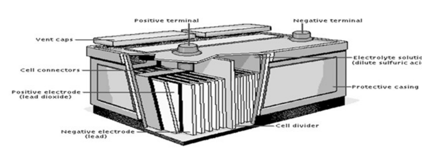
A rechargeable electric cell that converts chemical energy into electrical energy by a reversible chemical reaction & also called storage cell. Its of two types:

1) **Lead-Acid Battery**
2) Nickle-Metal Hydride Cell

Lead-Acid Battery

It's a secondary storage battery and in charged condition can be represented as

$Pb\ /\ PbSO_4\,(s)\ H_2SO_4\,(aq)\ //\ PbSO_4\,(s)\ PbO_2\,(s)\ /\ Pb$



The anode of the cell is a grid filled with spongy Lead, while cathode is Lead-Antimony grid containing PbO_2. The anode and cathode are separated by using porous material between them.
The electrolyte is 28-30% H_2SO_4 (Specific gravity = 1.2 at 25° C).

The whole set up of number of such cells are enclosed in a ebonite case.

Discharge Reaction of Lead-Acid Battery

During the discharge process of a battery the free energy change of redox reaction converted into electrical energy.

i.e. $\Delta G = - nFE$

Anodic Reaction

$Pb \longrightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$ ~ $E^o_{Pb/\ Pb2+} = - 0.36$ V

Cathodic Reaction

$PbO_2 + 4\ H^+ + SO_4^{2-} + 2e^- \longrightarrow Pb^{2+} + 2\ H_2O$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 + 2\ H_2O$

$PbO_2 + 4\ H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2\ H_2O$

~ $E^o_{PbO2/\ PbSO4} = 1.69$ V

Net Cell Reaction

$Pb + PbO_2 + 2\ H_2SO_4 \longrightarrow 2\ PbSO_4 + 2\ H_2O$

~ $E_{cell} = 2.0$ V

The voltage produced during discharging process is 2 V. The Lead Sulphate formed during the discharging process get adhere to the electrodes. The Lead Sulphate deposited on the electrode interface is utilised again during the charging process of the battery.

During the discharging, water is formed which dilutes H_2SO_4. With the decrease in concentration H_2SO_4 the density of the solution also decreases.

Charging Reaction of Lead-Acid Battery

The battery can be recharged by connecting it to an external source of direct current with voltage greater than 12 Volt. It forces the electrons to flow in opposite direction resulting in the deposition of 'Pb' on anode and PbO_2 on cathode.

The battery need charging when the specific gravity of H_2SO_4 acid falls below 1.2 & during recharging it behaves as electrolytic cell.

Anodic Reaction

$PbSO_4\,(s) + 2\ H_2O \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2e^-$

Cathodic Reaction

$PbSO_4\,(s) + 2e^- \longrightarrow Pb + 2\ SO_4^{2-}$

Overall Reaction

$2\ PbSO_4\,(s) + 2\ H_2O \longrightarrow Pb\ (s) + PbO_2 + H_2SO_4$

Lead storage battery is used in automobiles, UPS, telephone exchange, trains, laboratories.
The main disadvantage of Lead storage batteries is they cause environmental hazard & harmful for the human beings.

Secondary (Rechargeable) Lithium Batteries

Lithium batteries are of high energy density, power density, good life cycle, charge retention, high performance, reliable and safe.

The secondary Lithium batteries are classified into five categories-

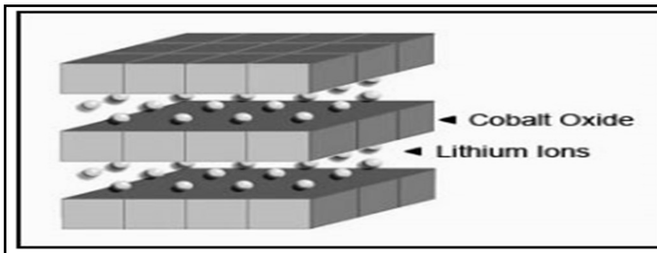
1) **Liquid Organic Electrolyte Cells**
2) Polymer Electrolyte Cells
3) **Lithium Ion Cells**
4) Inorganic Electrolyte Cells
5) Lithium Alloy Cells

Liquid Organic Electrolyte Cells ($LiCoO_2$)

It is a solid cell uses intercalation (Reversible inclusion or insertion of a molecule or ion materials with layered structure) for cathode, a liquid organic electrolyte and metallic lithium anode.

The battery consists of a cobalt oxide cathode and a graphite carbon anode. The cathode has a layered structure and during discharge, lithium ions move from the anode to the cathode. The flow reverses on charge.

The drawback of Li-cobalt is a relatively short life span, low thermal stability and limited load capabilities (specific power).



Its high specific energy makes Li-cobalt the popular choice for mobile phones, laptops and digital cameras.

Following material is used for the construction of the cell:

a) Anode: Lithium Metal
b) Cathode: $LiCoO_2$, $LiNiO_2$, MnO_2, V_2O_5
c) Electrolyte: $LiAsF_6$
d) Separator: Polypropylene

Anodic Reaction
$Li \longrightarrow Li^+ + e^-$
Cathodic Reaction
$Li^+ + LiCoO_2 + e^- \longrightarrow LiCoO_2$

Lithium Ion Cell (LiC_6)

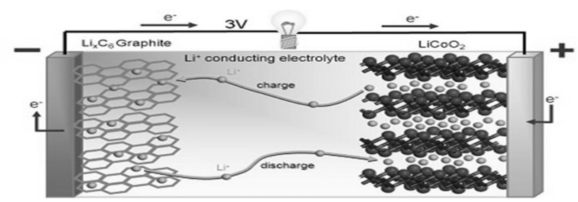
Lithium Ion Battery (LIB) has high energy density. The cell reaction in LIB is merely the migration of Lithium ions between anode and cathode.

No chemical changes are observed in the two electrodes or electrolytes.

Graphite has layered structure and can be doped with Lithium between the layers so its also known as Graphite Intercalation Compound.

Lithium doping is a charging reaction and undoping reaction is a discharging.

During charging of LIB, Lithium ions are extracted by electrochemical oxidation from $LiCoO_2$ cathode and extracted Lithium ions are doped by electrochemical reduction into carbon anode to form LiGIC.



During discharging Lithium ions are extracted from the anode by electrochemical oxidation and inserted into cathode by electrochemical reduction.

Anode oxidation reaction:
$LiC_6 \rightarrow Li^+ + C_6 + e-$
Cathodic reduction reaction:
$CoO_2 + Li^+ + e- \rightarrow LiCoO_2$
Overall reversible, Redox, cell reaction:
$LiC_6 + CoO_2 \longrightarrow C_6 + LiCoO_2$

The voltage of LIB is 3.6-3.7V.

Fuel Cell

Fuel cell is a device which convert chemical energy of the fuel into electrical energy. It is environmentally friendly potable power supplies capable of producing enough energy to run a device and motor vehicles.

These are voltaic cell in which the fuels such as H_2 , CO, CH_4 and C_3H_8 are used to generate electrical energy without the usage of thermal devices like boiler, turbines etc.

Fuel cells are designed in such a way that material to be oxidised and reduced at the electrodes are kept outside the cell and are constantly supplied to the electrodes & hence it do not require charging.

Fuel cells is a flow battery that continues to operate as long as the reactants from outside are fed into it.

Fuel |Electrode |Electrolyte |Electrode |Oxidant
At anode oxidation takes place and reduction takes place at cathode.

The working principal of fuel cell is the conversion of free energy change of redox reaction into electrical energy.

Types of Fuel Cells

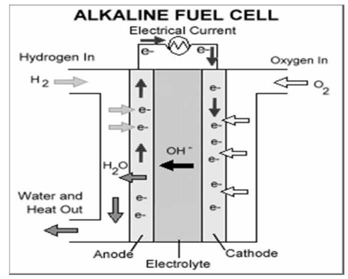
1) **Alkaline Fuel Cell (AFC)**
2) Phosphoric Acid Fuel Cell (PAFC)
3) Molten Carbonate Fuel Cell (MCFC)
4) Polymer Electrolyte Membrane Fuel Cells (PEMFC)
5) Solid Oxide Fuel Cell (SOFC)
6) Biochemical Fuel Cell (BCFC)

Alkaline Fuel Cell (AFC)

In alkaline fuel cell liquid electrolyte like NaOH / KOH is used. Pure Oxygen or air (free from CO_2) is used as oxidant. The fuel of the cell are hydrogen or any hydrocarbon.

Low temperature AFC operate at 60-80º C & highly active catalyst like Platinum or Ag are used. Catalyst like Ni require high temperature 200-250º C.

H_2-O_2 cell generates a voltage of 1.15V as long as the supply of H_2 & O_2 is maintained.



H_2-O_2 cell

Electrodes: Porous Carbon or Graphite
Electrolyte: KOH
Fuel: Hydrogen or Hydrocarbon
Catalyst: Platinum
Charge Carrier: OH-
Operating Temperature: 60-80º C

In AFCs, the oxygen reacts at the cathode to produce either hydroxide (OH^-) or a carbonate ion (CO_3^{2-}), depending upon the electrolyte composition. The ion travels through the electrolyte to react with hydrogen at the cathode.

Anodic Reaction
$H_2 + 2\,OH^- \longrightarrow H_2O + 2e^-$
Cathodic Reaction
$\frac{1}{2}\,O_2 + H_2O + 2e^- \longrightarrow 2\,OH^-$
Overall Reaction
$H_2 + \frac{1}{2}\,O_2 \longrightarrow 2\,H_2O$

Application:
Used in US space programme (Apollo Space programme) to produce electrical energy and water on-board spacecraft.