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UNIT-II
ENERGY CONVERSION AND STORAGE

(From the Academic year 2022-23 onwards)

Introduction: The conversion of chemical energy into electrical energy is the function of a cell or battery. A cell designates a single unit. A battery is a compact device consisting of two or more galvanic cells connected in series or parallel or both. It can store chemical energy in the form of active materials and on demand convert it into electrical energy through electrochemical redox reaction. Thus, a battery acts as portable source of electrical energy. Battery technology has acquired importance in view of development in microelectronics and increased demand for portable gadgets. Batteries are used in calculators, digital watches, pace makers, hearing aids, portable computers, electronically controlled cameras, car engines, stand-by power supplies, emergency lighting, and electroplating, industrial traction, telecommunication and military and space applications. Battery technology has made possible replacement of petrol driven automobiles by electrically powered ones. Electronic gadgets have become more reliable with the use of rechargeable batteries. A battery is designed and manufactured for a specific performance for example, to power a torch, to start a car engine, to supply emergency power to a hospital or to generate a very precise voltage to maintain heartbeats.

Components of a Battery

The basic electrochemical unit in a battery is a galvanic cell. The major components of a battery are described below and are selected based on the following properties.

1. Anode or negative electrode

i) It releases electrons to the external circuit by undergoing oxidation during electrochemical reaction. (Low reduction potential)
ii) It must be a good reducing agent.
iii) Capacity to deliver high coulombic output.
iv) It must possess good conductivity.
v) It must have high stability.
vi) It must be fabricated with ease.

2. Cathode or positive electrode

i) It accepts electrons from the external circuit and reduction of an active species occurs. (High reduction potential)

ii) It must be a good oxidizing agent.

iii) Good ionic conductivity.

iv) It must have high stability

3. Electrolyte

i) It must have good ionic conductivity but not to be electrically conductive, as this would cause internal short circuiting.

ii) It is the active mass in the anode and cathode compartments. The electrolyte is typically a liquid such as water or other solvents and a solution of an acid, alkali or salt having high ionic conductivity. Solid electrolytes with appreciable ionic conductivity at the operating temperature of the cell are also used.

iii) It should be safe in handling.

iv) It should be available at low cost.

v) Resistance to the electrode materials.

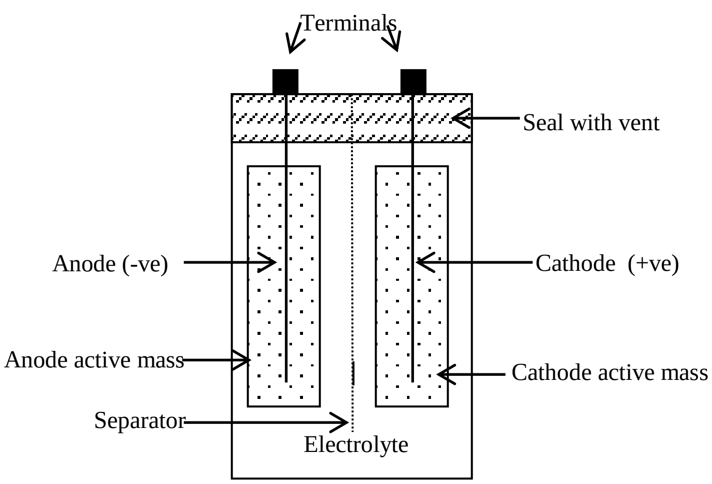
4. Separator

i) It separates the anode and the cathode in a battery to prevent internal short-circuiting.

ii) It is permeable to ions and maintains the desired ionic conductivity.

iii) The main function of the separator is to transport ions from the anode compartment to the cathode compartment and vice versa. Fibrous forms of regenerated cellulose, vinyl polymers, and polyolefins, cellophane and nafion membranes are used as separators.

iv) High capacity to prevent mixing of active masses in the two compartments



The anode and the cathode are surrounded by the respective active masses. The electrodes are separated by a suitable separator to prevent internal short-circuiting. It is sealed to prevent leakage and drying out. A few cells are provided with vents to allow accumulated gaseous products to escape.

Operation of a Battery

The operation of a battery involves discharge (delivering power) and recharge in the case of storage battery.

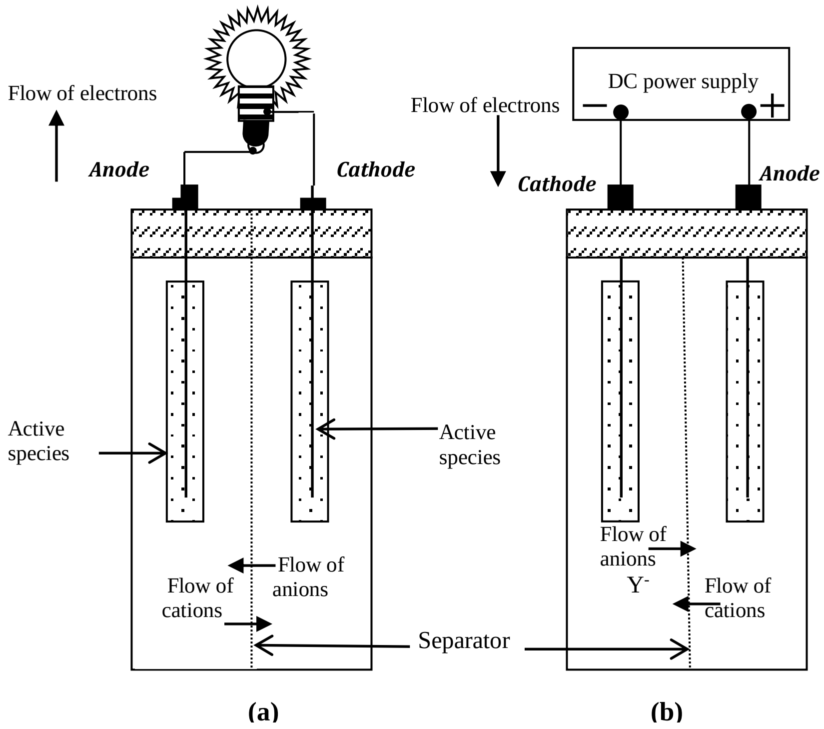


Figure (a) Discharge of a battery (b) Recharge of a battery

Discharge: Discharge occurs when the battery is connected to an external circuit and the circuit is closed as shown in Figure (a).

During discharge, the anode undergoes oxidation to form cations and release electrons. The electrons flow from the anode to the cathode through the external circuit. At the cathode, electrons are accepted and the active species at the cathode compartment is reduced to form anions. The anions and cations formed at the respective electrodes move across the separator to maintain electro neutrality and to complete the electric circuit.

Assume a metal **M** as the anode material and **A** as the cathode material.

The reactions occurring during discharging are as follows.

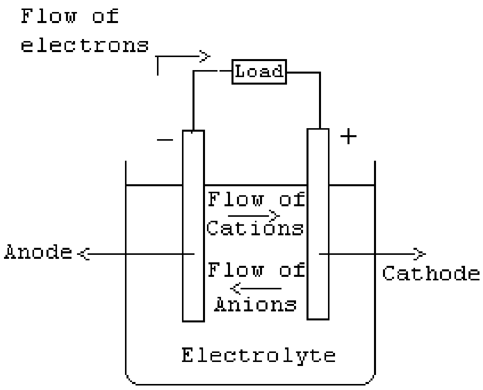
Negative electrode: Anodic reaction (oxidation, loss of electrons)

$$M \rightarrow M^{n+} + ne$$

Positive electrode: Cathodic reaction (reduction, gain of electrons)

$$A + ne \rightarrow A^{n-}$$

Overall reaction during discharge: $M + A \rightarrow M^{n+} + A^{n-}$



Recharge: (Charge)

During recharge, the current flow is reversed with the aid of a dc power supply. The negative terminal of the power supply is connected to the negative electrode of the battery and the positive terminal of the power supply to the positive electrode of the battery as shown in Figure (b). At anode the active species is reduced to metal and at cathode, oxidation takes place forming the active species. Thus, during recharge, the positive electrode is the anode and the negative electrode is the cathode. The electrode reactions occurring during recharge are the reverse of those occurring during discharge.

The reactions occurring during charging are as follows.

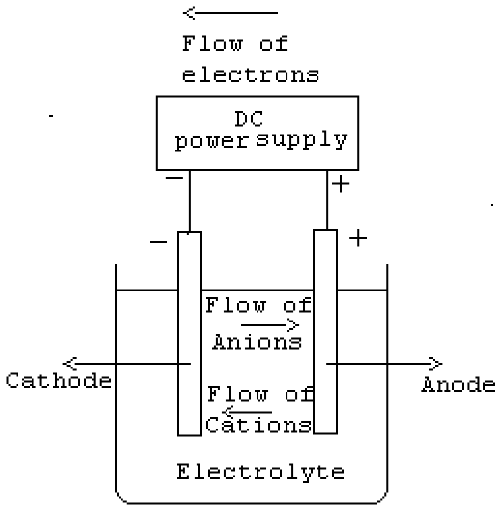
Negative electrode: Cathodic reaction (reduction, gain of electrons)

$$M^{n+} + ne \rightarrow M$$

Positive electrode: Anodic reaction (oxidation, loss of electrons)

$$A^{n-} \rightarrow A + ne$$

Overall reaction during charge: $M^{n+} + A^{n-} \rightarrow M + A$



Classification of Batteries

Batteries are classified as (i) primary batteries (ii) secondary batteries and (iii) Reserve batteries

Primary batteries: In primary batteries the cell reactions are not reversible. They are not rechargeable and once discharged have no further electrical use.

Eg: Zn-MnO_2 battery and Li-MnO_2 battery.

Secondary batteries: In secondary batteries the cell reactions are reversible. They are also called storage batteries. The cell once discharged, can be recharged by passing current through it in the direction opposite to that of discharge current. These are storage devices for electrical energy and referred as storage batteries or accumulators.

Eg: Lead storage battery and nickel-cadmium battery.

Reserve batteries: The batteries, which may be stored in an inactive state and made ready for use by (by adding an electrolyte, another cell component) activating them prior to application are referred to as reserve batteries.

In reserve batteries one of the key components is separated from the rest of the batteries prior to activation and hence the battery is capable of long term storage. Usually, the electrolyte is stored separately.

Eg: Magnesium batteries activated by water (Mg-AgCl and Mg-CuCl)

Zn-Ag_2O batteries

Reserve batteries have the following advantages:

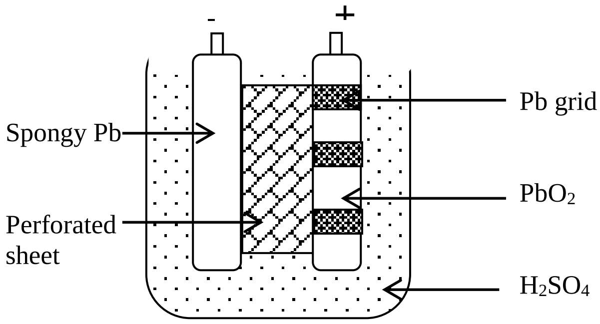
(i) Long shelf life (ii) High performance reliability (iii) Variety of design options.

Reserve batteries are primarily used to deliver high power for relatively short periods of time in applications such as radio sensors (air borne instruments to send meteorological information back to earth by radio), missiles, mid-ocean disasters and crisis in space.

Classical batteries

1. Lead- acid battery

The practical lead acid batteries came into existence with the research of Raymond Gaston Plante in 1860. Lead acid storage battery consists of six identical cells joined together in series. The lead storage battery consists of two electrodes made of flat grids of lead.



Anode: The anode grid is packed with a paste consisting of spongy lead and additives such as carbon powder (0.25%) lignin sulphonate (0.2%) and barium sulphate (0.35%). The graphite improves the conductivity while the other additives prevent the reduction in the surface area of the lead.

Cathode: The cathode lead grid is packed with a paste consisting of equal amounts of PbO_2 and Pb.

Electrolyte: Anode-cathode grids are immersed in an aqueous solution of sulfuric acid (38%) which acts as the electrolyte.

Separator: Separators made of microporous polyethylene or resin impregnated papers are used in between each set of electrodes to insulate each plate from its neighbouring counter electrode. The separators, however, allow acid transport into and out of the plates.

The intercell connectors and terminals are welded into place and sealed. The battery is encased in a plastic or glass container.

The cell is represented as Pb, $PbSO_4$ (s)|H_2SO_4 (5M)| $PbSO_4$(s), PbO_2(s), Pb

The chemistry during discharge and charge is as follows.

$$\text{At anode: } Pb(s) + SO_4^{2-}(aq) \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4(s) + 2e$$

$$\text{At cathode: } PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4(s) + 2H_2O(l)$$

$$\text{Overall reaction: } Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O(l)$$

Performance: Each pair of electrodes produces 2V and a battery consisting of six such electrode pairs gives about 12 V.

Capacity: 2.7 Ah

Energy density: 33 $Whkg^{-1}$

Weight: 150 g

Applications

i. Lead storage battery is used for starting, lighting and ignition (SLI) in cars, trucks, buses, tractors, small craft, light aeroplanes and in motor generators, standby system.

ii. Industrial lead acid batteries find applications in various kinds of traction, example mine haulage, standby power applications such as telecommunications, heavy duty engine starting.

iii. Sealed lead acid batteries are in the security and alarm systems, emergency lighting and uninterrupted power supplies (UPS).

2. Nickel-cadmium battery

In this battery the electrodes are made from perforated nickel plated steel strips.

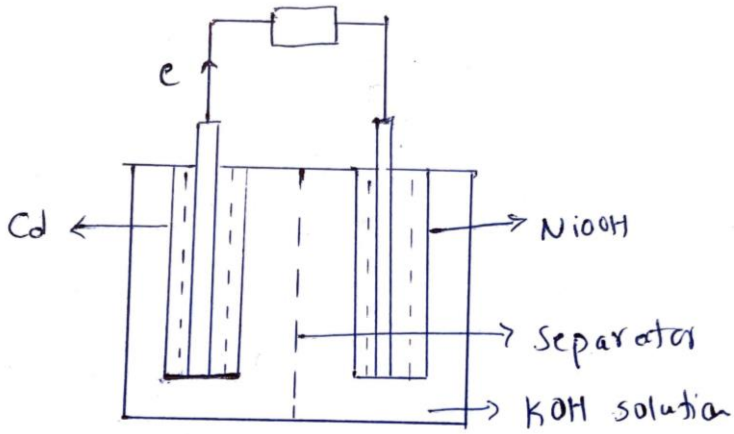
Anode: The active material for the anode (-ve) is a mixture of 78% cadmium hydroxide, 18% iron 1% nickel and 3% graphite dry mixed, powdered and pressed. Iron, nickel and graphite are added to reduce ball-up, i.e., changes in the morphology leading to loss in active surface area of cadmium.

Cathode: The active material for the cathode (+ve) is a mixture of nickel oxyhydroxide (80%), cobalt hydroxide (2%), graphite (18%) and with a trace amounts of barium compound. Graphite is added to improve the conductivity, while cobalt and barium compounds increase the percentage usage of active material during the discharge and also increase the cycle life.

The active materials are filled into pocket plates (two perforated nickel coated steel strips) and connected in series as shown in Figure.

Electrolyte: 6 M KOH (3%)

Separator: The plates are separated using a very thin insulator.



The nickel-cadmium (NiCad) cell is represented as

$Cd(s), Cd(OH)_2(s)|KOH\ (6\ M)\ |\ Ni(OH)_2(s), NiO(OH)(s)$

The half-cell reactions are

$$Cd(s) + 2OH^-(aq) \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Cd(OH)_2\ (s) + 2e \quad \ldots \text{anode}$$

$$2NiO(OH)(s) + 2H_2O + 2e \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2Ni(OH)_2(s) + 2OH^-(aq) \quad \ldots \text{cathode}$$

The net cell reaction is

$$Cd(s) + 2NiO(OH)(s) + 2H_2O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2Ni(OH)_2\ (s) + Cd(OH)_2\ (s)$$

Applications

i. The use of pocket -plate batteries is in emergency lighting, electrical switch gear, railway track and signal applications, heavy duty engine cranking.

ii. Sintered type batteries find use in cordless tools and pocket calculators.

Modern batteries

3. Zinc-air battery

Anode: The anode consists of rectangular flat plates of zinc placed on either side of the cathode.

Cathode: It consists of a porous carbon plate as cathode, through which air (O_2) is passed. The cathode is activated for better reduction of oxygen.

Electrolyte: The electrolyte is 20% NaOH (5M).

The outer container is made of glass or ebonite. Zinc-air battery is an example of rechargeable battery. Its advantage is that air does not contribute to the mass of the battery hence offers high energy density.

The cell is represented as,

$$Zn \mid NaOH\ (5M) \mid air, C$$

When air is passed through the cell, zinc is oxidized to ZnO at the anode, during discharge. The oxygen of the air reacts with water at the cathode.

The half-cell reactions are

$$2Zn + 4OH^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2ZnO + 2H_2O + 4e \qquad \ldots \text{ anode}$$

$$O_2 + 2H_2O + 4e \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 4OH^- \qquad \ldots \text{ cathode}$$

The overall reaction is

$$2Zn + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2ZnO$$

Zn-air battery is has an energy density of about 100 W h kg^{-1}. This is three times that of the classical lead acid battery and twice that of Nicad battery.

Applications

Zn-air battery finds applications in railways and military radio receivers.

Lithium Batteries

Lithium has the following characteristics.

i) It has light weight.

ii) It has high electrochemical equivalence (3.86 A h g^{-1}).

iii) It has good electrical conductivity.

iv) It has high standard electrode potential (-3.05 V).

These features have made lithium useful as anode material for battery construction. Electronic gadgets demand batteries with high energy density, high energy efficiency, high voltage and long life cycle. In this regard, lithium has been used in the development of high performance primary and secondary batteries.

4. Li-MnO_2 cell

Anode: Lithium

Cathode: Specially prepared heat-treated MnO_2

Electrolyte: Lithium salt (LiCl, LiBr, $LiClO_4$, $LiAlCl_4$ or $LiCF_3SO_3$) dissolved in a mixed organic solvent (propylene carbonate and 1,2-dimethoxyethane).

Separator: anode and the cathode are separated by a non-woven polypropylene membrane.

The half-cell reactions occurring during discharge are

$$Li \longrightarrow Li^+ + e \quad \text{… anode}$$

$$MnO_2^{IV} + Li^+ + e \longrightarrow MnO_2^{III}(Li^+) \quad \text{… cathode}$$

The overall reaction is $MnO_2^{\ IV} + Li \longrightarrow MnO_2^{\ III}(Li+)$

Formation of $MnO_2^{\ III}(Li^+)$ indicates that Li^+ ion enters the MnO_2 crystal lattice. The cell gives a voltage of 3.0 V and an energy density of 230 Wh/kg. Li-MnO_2 battery is available in many configurations such as coin, bobbin, spirally wound, cylindrical and prismatic.

Applications

Li-MnO_2 battery is used in memory backup, safety and security devices, watches, calculators, automatic cameras and many consumer electronic devices.

5. Lithium ion battery

Lithium ion is a rechargeable battery has the following advantages:

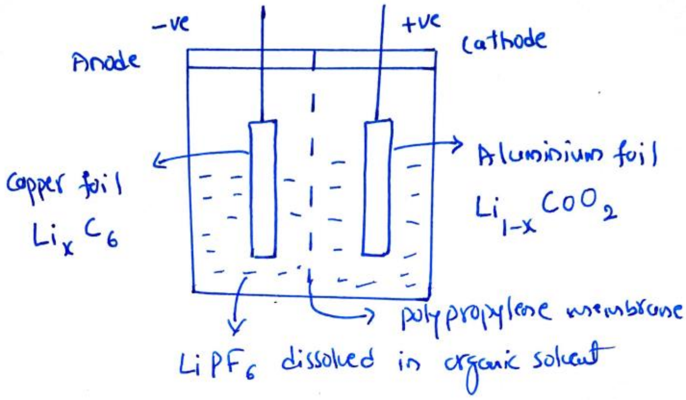
i. It is light in weight.
ii. It gives high voltage.
iii. Battery performance is good.
iv. It has long life.
v. It operates at wide range of temperature from -20 ^oC to 40 ^oC. Hence, used in the manufacture of mobile electronic devise.

Anode: Lithium intercalated graphite/carbon such as Li_xC_6 pasted to copper foil.

Cathode: Partially lithiated oxides of Co or Ni such as $Li_{1-x}CoO_2$ pasted to aluminium foil.

Electrolyte: $LiPF_6$ dissolved in organic solvent such as propylene carbonate or ethylene carbonate.

Separator: Anode and cathode are kept in a steel or Al-alloy container and separated by micro porous polypropylene membrane.



The half-cell reactions occurring during discharge are

$$Li_xC_6 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} xLi^+ + xe^- + 6C \qquad \text{… anode}$$

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} LiCoO_2 \qquad \text{… cathode}$$

The overall reaction is

$$Li_xC_6 + Li_{1-x}CoO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 6C + LiCoO_2$$

Applications:

Li-ion batteries are used in cell phones, LCD TV's, laptops, cameras, CD players.

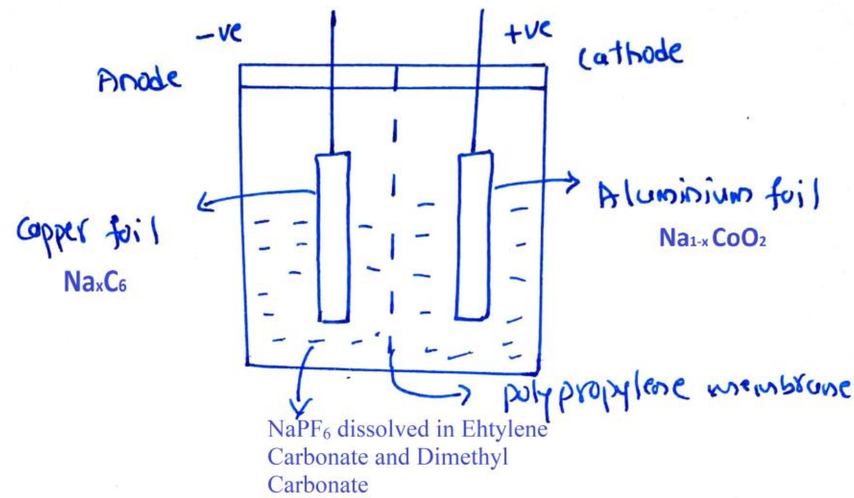
NOTE: Batteries are incredibly useful in modern technology. The commonly used lithium ion batteries are considered to be relatively eco-friendly, when compared to lead-acid batteries and other alternatives, and are much better for the environment. These contain less toxic metals than other batteries. Many modern batteries contain chemicals like nickel, cobalt, lead, cadmium and mercury. These substances make disposing of batteries difficult. These lithium ion batteries can be ethically and environmentally problematic since only a small percentage of lithium ion batteries are recycled. Hence, Sodium-ion batteries have become a more environmentally friendly alternative to lithium-ion batteries. They are cheaper and more sustainable, since in the earth's crust, there is more than 1000 times more sodium than lithium.

6. Sodium-ion batteries (Na-ion batteries or NIBs)

Sodium-ion battery is a type of rechargeable battery that uses sodium ions (Na^+) as its charge carriers. Its working principle and cell construction are almost identical with those of lithium-ion battery types, but replace lithium with sodium. Sodium-ion batteries are a potential alternative to lithium-based battery technologies, largely due to sodium's lower cost and greater availability. Since Sodium-ion battery use abundant and cheap materials, they are expected to be less expensive than Lithium-ion battery. The environmental impacts of Sodium-ion battery are also lower. Although Sodium-ion battery is heavier and larger than Lithium-ion battery, they are feasible for stationary energy storage systems where the weight and volume are less crucial.

The largest advantage of sodium-ion batteries is the natural abundance of sodium. Challenges to adoption of SIBs include low energy density and insufficient charge-discharge cycles.

Construction and working



Anode: Na_xC_6 coated on Copper foil

Cathode: $Na_{1-x}CoO_2$ coated on Aluminium foil

Electrolyte: $NaPF_6$ dissolved in Ehtylene Carbonate and Dimethyl Carbonate

Separator: Polypropylene membrane

The half-cell reactions occurring during discharge are

$$Na_xC_6 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} xNa^+ + xe^- + 6C \quad \ldots \text{ anode}$$

$$Na_{1-x}CoO_2 + xNa^+ + xe^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} NaCoO_2 \quad \ldots \text{ cathode}$$

The overall reaction is

$$Na_xC_6 + Na_{1-x}CoO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 6C + NaCoO_2$$

Applications

A growing focus on cost-effective advanced storage technologies is encouraging the use of sodium-ion batteries in several sectors, such as transportation, consumer electronics, industrial, large-scale stationary energy storage.

Advantages of NIBs

- Sodium-ion batteries offer better performance and can operate at a wider temperature range.
- NIBs work efficiently in cold environments, compared to lithium-ion batteries.
- **S**odium-ion batteries are non-flammable**.**

Questions:

1. What is a battery? Discuss the classification of batteries with an example.
2. Explain the operation of a battery during charging and discharging process.
3. Discuss the principal components of a battery.
4. Explain the construction and working of Lead-acid storage battery.
6. Discuss the construction Nickel-Cadmium and Li-ion batteries.
7. Mention the anode, cathode and electrolytes used in the following batteries. Write the anodic and cathodic reactions involved: (i) Zinc - air battery (iii) Li-MnO_2 battery.
8. Mention the electrode reactions and applications of Na-ion batteries.

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