UNIT II - Clean Energy Storage and Conversion Devices

Syllabus: Introduction to electrochemistry, basic concepts of Batteries and characteristics. Classification: Primary (Dry cell, Li-MnO₂) and Secondary (Pb-acid, Li-ion) batteries. Super capacitors: classification, construction and applications in hybrid vehicles. Fuel cells: Alkaline fuel cells, Solid oxide fuel cells and phosphoric acid fuel cell. Photo-conversion devices: Photovoltaic cell, antireflective coating, panels and arrays. Production of single crystal semiconductor by Crystal pulling technique (Czochralski technique), zone refining process of Si. Problems: Calculation of energy and power density, capacity of a Battery and capacitance of super capacitors for electric vehicle applications.

Introduction and basic concepts

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction. In the case of a rechargeable system, the battery is recharged by reversal of the process. This type of reaction involves the transfer of electrons from one material to another through an electric circuit. As the battery electrochemically converts chemical energy into electric energy, it is not subject, as are combustion or heat engines, to the limitations of the Carnot cycle dictated by the second law of thermodynamics. Batteries, therefore, are capable of having higher energy conversion efficiencies. While the term "battery" is often used, the basic electrochemical unit being referred to is the "cell." A battery consists of one or more of these cells, connected in series or parallel, or both depending on the desired output voltage and capacity.

Components of a battery

- 1. The anode or negative electrode: It is a reducing electrode, which is susceptible to oxidation and produce electrons which flow through external circuit. In a practical system/cell, the anode is selected with the following properties in mind: efficiency as a reducing agent, high coulombic output (Ah/g), good conductivity, stability, ease of fabrication, and low cost. Practically, metals are mainly used as the anode material. Lithium, the lightest metal, with a high value of electrochemical equivalence, has become a very attractive anode as suitable and compatible electrolytes and cell designs have been developed to control its activity.
- 2. The cathode or positive electrode: It is an oxidizing electrode, which accepts electrons from the external circuit and at which reduction reaction leads to deposition/liberation of a compound. The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage. Oxygen can be used directly from ambient air being drawn into the cell, as in the zinc / air battery. However, most of the common cathode materials are metallic oxides. Other cathode materials, such as the halogens and the oxyhalides, sulfur and its oxides, are used for special battery systems.
- 3. The electrolyte; It is an ionic conductor which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode. Generally an electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalis to influence ionic conductivity. Some batteries use solid electrolytes, which are ionic conductors at the operating temperature of the cell. The electrolyte must have good ionic conductivity but not be electronically conductive, as this would cause internal short-circuiting. Other important characteristics are non reactivity with the electrode materials, little change in properties with

change in temperature, safety in handling, and low cost. Most electrolytes are aqueous solutions, but there are important exceptions as, for example, in thermal and lithium anode batteries, where molten salt and other non aqueous electrolytes are used to avoid the reaction of the anode with the electrolyte. The most preferable combinations of anode and cathode materials are those that will be lightest and give a high cell voltage and capacity. Such combinations may not always be practical, however, due to reactivity with other cell components, polarization, and difficulty in handling, high cost, and other deficiencies. Zinc has been a predominant anode because it has these favorable properties. Lithium, the lightest metal, with a high value of electrochemical equivalence, has become a very attractive anode as suitable and compatible electrolytes and cell designs have been developed to control its activity.

4. Separator: Physically the anode and cathode electrodes are electronically isolated in the cell to prevent internal short-circuiting, but are surrounded by the electrolyte. In practical cell designs a separator material is used to separate the anode and cathode electrodes mechanically. The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity. In some cases the electrolyte is immobilized using gelling agents. To reduce internal resistance, some electrically conducting grid structures or materials may also be added to the electrodes.

Battery characteristics

1. Voltage

The voltage of a battery is a fundamental characteristic of a battery, which is determined by the chemical reactions in the battery that is free energy change in the over all reactions which in turn depends on electrodes, the concentrations of the battery components, and the polarization of the battery. Voltage of a battery is given by;

$$E_{cell} = (E^o_C - E^o_A) - \eta_A - \eta_c - iR_{cell}$$

From the above expression we can conclude that;

- a) Higher the standard reduction potential difference between the electrodes employed, higher the voltage.
- b) Lower the internal resistance higher the battery voltage. For this to happen a high conducting electrolyte must be chosen and electrodes should be kept at optimum distance (cell design).
- c) The electrode overpotentials must be low for higher battery voltage.
- d) Also the temperature affects the battery voltage, as temperature increases voltage of the battery decreases according to the equation;

$$E_{cell} = E^O_{cell} - 2.303RT/nF \ log \ Q$$

Where 'Q' is the reaction quotient, the ratio of product of molar concentration of products to that of reactants.

2. Current

It is a measure of rate at which battery discharges. For the ability to deliver high current without much voltage expense, depends on the fast electron transfer. This is possible when design of the

active material is precise (therefore the active materials are taken in the form of a porous material).

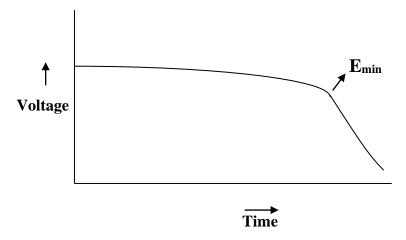
3. capacity

Capacity of a battery is the charge that may be obtained from the battery under specified discharge conditions, before its voltage drops to an unsatisfactory level. It is expressed in terms of Ampere-hour (1Ah = 1 A flowing for 3600 seconds, i.e. 1 Ah = 3600 coulombs) and it depends on the size of battery. Capacity of each electrode (Active material) can be calculated from the weight 'W' of the active material using Faraday's law;

$$C = WnF / M$$

Where; M = Molar mass of active material and W= Mass of active material

The practical capacity of each electrode and hence of the battery depends on how much active material consumed during discharge and discharge conditions. A graph of battery voltage and time at a fixed current discharge indicates the capacity of a battery. The length of flat portion is a measure of the capacity of a battery; longer the flat portion higher the capacity of the battery and E_{min} is the value of voltage at which battery is said to be dead.



4. Cycle life

It is the number of charge - discharge cycles that are possible before failure of a secondary battery occurs. In a secondary battery the products formed during discharge must be available for charging which in turn decides cycle life of a battery. The common reasons for a poor cycle life of a battery are;

- a) Corrosion at contact points
- b) Shedding of active materials from the electrode plates
- c) Leakage of electrolyte
- d) Cycle life decreases with increased depth of discharge
- e) Short circuit between electrodes due to the irregular growth of salts on electrode plates

5. Energy density (By weight and volume)

It is the amount of energy that can be extracted from a unit weight/volume of a battery. The *Energy density by weight* is a measure of how much energy a battery contains in comparison to its weight. The *Energy density by volume* is a measure of how much energy a battery contains in comparison to its volume. We know that electrochemical energy is given by;

Electrochemical energy = quantity of electricity x potential difference

$$= (I x t) x V_e$$

$$= q \times V_e$$
 where 'q' is the charge $= I \times t$

Therefore Energy density = charge $X V_e$ / weight ----- wh/kg Also Energy density = charge $X V_e$ / volume ----- wh/L

6. Power density

It is the power available per unit weight of a battery. Also it can be defined as the ratio of the power delivered to its weight. During discharge power density decreases.

Power = I x
$$V_{work}$$

Therefore Power density = I x V_{work}/W ----- W/kg

7. Energy efficiency

The energy efficiency of a battery is expressed in percentage and is given by;

% Energy efficiency = Energy given out during discharge / Energy required for charge X 100 The % Energy efficiency depends on the rate of charge and discharge conditions. It also depends on the reactions that take place during both conditions and internal resistance of the battery also affect % Energy efficiency.

8. Shelf life

The duration of storage under specified conditions at the end of which a battery still has effective discharging capacity is called its shelf life. For example; when dry cell is stored at a temperature 21°C for a period of time (measured from the date of manufacture), it still shows 90% energy of its original energy content.

Classification of batteries

Batteries are classified into three types namely;

- a) Primary batteries b)Secondary batteries
- c) Reserve batteries

a) Primary batteries

These are the class of batteries in which electrical energy can be obtained at the expense of chemical energy as long as the active materials are present and the reactions are irreversible. $Example: Zn - MnO_2 dry cell, Zn - air battery, Alkaline - Manganese battery, Lithium - sulphur dioxide battery, Lithium - Thionyl chloride battery and Li - <math>MnO_2$ battery etc.

b) Secondary batteries

The type of batteries which convert chemical energy into electrical energy during discharge and they can be restored through charging process. The reactions are reversible, hence they are also known as 'Storage batteries' or 'Rechargeable batteries'.

Example: Lead – acid battery, Ni – Cd battery, Ni – MH battery, Nickel – Hydrogen battery, Nickel – Iron battery, Lithium – ion battery etc.

c) Reserve batteries

"Batteries, which are designed for instantaneous application, without an inbuilt electrolyte and activated by adding electrolyte at the time of requirement, to eliminate self-discharge problem prior to use", are known as reserve batteries". Since the electrolyte is isolated from battery, the problem of self discharge is eliminated and the battery is capable of long term storage. These

batteries are exclusively used to deliver high power in a short period of time, in missiles, torpedoes and other weapon systems.

Example: Magnesium – water activated batteries, Zinc – silver oxide battery, and Li – $V_2 O_5$ battery etc.

Super capacitors

Electric/Electrochemical double layer capacitor (EDLC) also known as supercapacitors, is a unique electrical storage device. They can store much more energy than conventional capacitors and hence of higher power density than batteries.

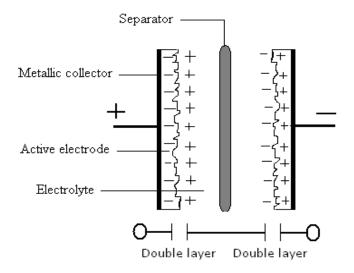
Principle

EDLC work on the principle of double layer capacitance at the electrode/electrolyte interface when electric charge accumulate on the electrode surface and the ions of opposite charge align on the electrolyte side.

Materials used in EDLCs

EDLCs consist of two electrodes in contact with an electrolyte, which are separated an ion permeable separator. Usually the electrodes of large surface area like porous carbon, graphene, carbon nanotubes and certain conducting polymers are employed so that more large number of charges can be stored.

Construction



Working

When a potential is applied between the electrodes, (-) ve ions move towards positive electrode and (+) ve ions move towards negative electrode. As a result this electric double layer is formed and charges stored. Unlike batteries the storage of charges takes place in supercapacitors by static electricity. The capacity of a supercapacitor depends on the active electrode area, increasing the area increases capacity of supercapacitor. For this reason porous materials are used as electrode active materials.

Nature of electrode

Combination of a highly conducting metal collector and an active material of high surface area separated by an ion permeable separator, acts as electrode. This composite is rolled or folded into cylindrical or rectangular shape and immersed into an electrolyte.

Separator

If electrolyte is organic, a polymer or a paper separator is used. For an aqueous electrolyte, glass fiber or ceramic separator is used. The separator allows the transfer of the charged ions but forbids the electronic contact between the electrodes.

Electrolyte

Usually the electrolytes used are organic electrolytes, KOH, H₂SO₄ etc.

Advantages

- Long life, with little degradation over hundreds of thousands of charge cycles
- Extremely low internal resistance and high cycle life
- High output power
- Improved safety, i.e. no corrosive electrolyte and low toxicity of materials
- No full charge detection is needed and no danger of overcharging

Disadvantages

- Has highest dielectric absorption
- High self discharge the rate is considerably higher than that of an electrochemical battery
- Very low internal resistance allows extremely rapid discharge when shorted

Classical batteries

PRIMARY BATTERIES

The batteries in which the reactions are said to be irreversible, are called primary batteries and are designed for single discharge.

Example; Zn – MnO₂ dry cell

1. Construction, working and applications of Zn – MnO₂ battery

Active materials

The Zn- MnO₂ dry cell is comprises of the following active materials;

Anode: Zn - cylinder covered by a paste of $NH_4Cl + ZnCl_2$ which is immobilised by adding gelatin or starch

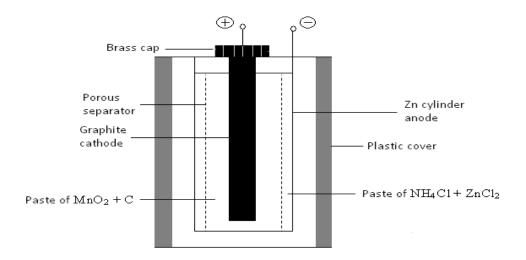
Cathode: Graphite rod covered by a paste of $MnO_2 + C$ paste

Cell voltage: 1.5volts

It is called dry cell because of no presence of liquid electrolyte.

Cell notation: Zn/Zn²⁺, NH⁺4/MnO₂, C +

Construction



The dry cell is comprised of a Zinc cylinder which acts as anode, is covered by a paste of ammonium chloride and zinc chloride to make battery spill proof, which is immobilised by the addition of gelatin or starch. A graphite rod placed at the centre acts as cathode provided with a brass cap for external contact as shown in the diagram and is covered by a paste of MnO₂ and carbon powder. Since the conductivity of MnO₂ is low, granulated carbon is added to increase the conductivity. The whole assembly is covered a plastic material to reduce leakage.

During discharge

Zinc undergoes oxidation at anode and at cathode Mn (IV) is reduced to Mn (III). The reactions are as follows;

Primary electrode reactions

At anode (-); $\operatorname{Zn} \longrightarrow \operatorname{Zn}^{2+} + 2e^{-}$

At cathode (+); $2MnO_2 + H_2O + 2e^- \longrightarrow Mn_2O_3 + 2OH^-$

Net cell reaction; $Zn + MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^{-}$

Secondary electrode reactions

The hydroxyl ions generated in primary reactions react with ammonium chloride and liberate ammonia which in turn reacts with Zn^{2+} forming a highly insoluble complex [$Zn(NH_3)_2Cl_2$].

$$2NH_4Cl + 2OH^- \longrightarrow 2NH_3 + 2H_2O + 2Cl^-$$

 $Zn^{2+} + 2NH_3 + 2Cl^- \longrightarrow [Zn(NH_3)_2Cl_2]$

The zinc ions formed in primary reactions are consumed in secondary reactions forming a highly insoluble complex [Zn(NH₃)₂Cl₂], as a consequence the reactions become irreversible and hence it cannot be recharged. The secondary reactions are not directly involved in electrode reactions, so they do not contribute to the cell emf.

Applications

Extensively used in; Flash lights, transistors, portable radios, tape recorders and toys

SECONDARY BATTERIES

The batteries, in which the reactions are said to be reversible, are called secondary batteries. Based on the nature of electrolyte, there are two types of storage batteries;

- 1) Acid storage batteries, Example; Lead-acid storage battery
- 2) Alkaline storage batteries, Example; Ni Cd battery

1. Construction, working and applications of Lead-acid storage battery

Active Materials

The lead - acid battery is made up of the following active materials;

Anode: Lead grids filled with spongy lead *Cathode:* Lead grids filled with lead oxide

Electrolyte: 27% to 35% Sulphuric acid (H₂SO₄), specific gravity; 1.250g/cm³

Separator: An inert porous separator (membrane) is placed between each pair of electrodes

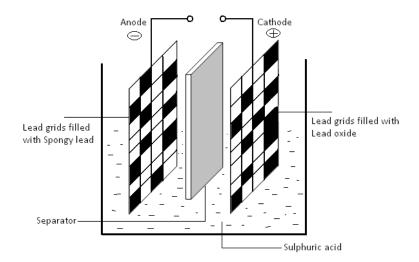
Example; Cellophane, Nafion, Polyvinylchloride etc.

Cell voltage: 2Volts per pair of electrodes

All these components are placed in proper leak proof container, usually made of plastic material.

Cell notation: Pb / PbSO_{4(s)}, H₂SO₄ // PbO_{2(s)}, PbSO_{4(s)}, / Pb

Construction



a) During Discharge

During discharge the lead - acid acts as galvanic cell, hence the reactions are spontaneous and the electrodes are;

Anode: Lead grids filled with spongy lead *Cathode:* Lead grids filled with lead oxide

Electrolyte: 27% to 35% Sulphuric acid (H₂SO₄), specific gravity; 1.250g/cm³

As the battery discharges, active materials in the electrodes (lead dioxide in the positive electrode i.e., cathode and spongy lead in the negative electrode i.e., anode) react with sulfuric acid in the electrolyte to form lead sulfate and water. The water formed reduces the specific gravity of acid to $1.18g/cm^3$ beyond which discharge should not be continued otherwise the battery is damaged permanently (Due to the formation of insoluble PbSO₄). The reactions that occur during discharge process are;

Reactions:

at anode (-);

Pb
$$\rightarrow$$
 Pb²⁺ + 2e⁻

Net anode reaction;
$$\frac{Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4}{Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^{-}}$$
 (1)

at cathode(+);

$$PbO_{2} + 4H^{+} \longrightarrow Pb^{4+} + 2H_{2}O$$

$$Pb^{4+} + 2e^{-} \longrightarrow Pb^{2+}$$

$$Pb^{2+} + SO_{4}^{2-} \longrightarrow PbSO_{4}$$
Net anode reaction;
$$PbO_{2} + 4H^{+} + 2SO_{4}^{2-} + 2e^{-} \longrightarrow PbSO_{4} + 2H_{2}O$$
(2)

The overall reaction for discharge process is (1) + (2)

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

b) During Recharge

During charging process lead sulfate on both electrodes converts back to lead dioxide (at anode) and spongy lead (at cathode). The sulfate ions (SO₄²⁻) driven back into the electrolyte solution react with H⁺ ions to form sulfuric acid. The battery is considered to be fully charged when the specific gravity of the acid reaches 1.250g/cm³.

Reactions

At anode:

$$PbSO_{4} \longrightarrow Pb^{2+} + SO_{4}^{2-}$$

$$Pb^{2+} \longrightarrow Pb^{4+} + 2e^{-}$$

$$Pb^{4+} + 2H_{2}O \longrightarrow PbO_{2} + 4H^{+}$$
Net anode reaction:
$$Pb^{2+} + 2H_{2}O \longrightarrow PbO_{2} + 4H^{+} + SO_{4}^{2-} + 2e^{-}$$
(3)

at cathode:

$$\begin{array}{ccc}
 & PbSO_4 \longrightarrow Pb^{2+} + SO_4^{2-} \\
 & \underline{Pb^{2+} + 2e^{-} \longrightarrow Pb} \\
 & PbSO_4 + 2e^{-} \longrightarrow Pb + SO_4^{2-}
\end{array} \tag{4}$$

The overall reaction for Recharge process is (3) + (4);

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

For the overall cell;

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4\,(aq)} \qquad \begin{array}{c} Discharging \\ \hline \\ Charging \end{array} \qquad 2PbSO_{4(s)} + 2H_2O_{\,(l)}$$

Therefore the maximum open-circuit voltage that can be developed by a single lead-acid cell is 2.041 V.

Applications

- Lead acid battery is used extensively in automobiles to start engines
- As a source of electricity in telephone exchangers, railways, hospitals and laboratories
- As an emergency power supply (UPS)

LITHIUM BATTERIES

Lithium metal has become the most attractive battery anodic material because of its light weight, high potential, high electrochemical equivalence, and good conductivity.

The advantageous features of Lithium batteries over conventional one are

- 1. High voltage: Lithium batteries have voltage up to 4V, depending on the cathode material.
- 2. *High energy density:* The energy output of a lithium battery is 2 to 4 times better than that of conventional zinc anode batteries.
- 3. Wide operating temperature range: Many of the lithium batteries will perform over a temperature range from about 70 to -40°C, with some capable of performance to 150°C or as low as -80°C.
- 4. Good power density
- 5. High flat discharge characteristics
- 6. Superior shelf life: Lithium batteries can be stored for long periods, even at elevated temperatures. Storage of up to 10 years at room temperature has been achieved and storage of 1 year at 70°C has also been demonstrated.

1. Construction, working and applications of Li – MnO₂ battery

Lithium – Manganese dioxide battery is an example for primary lithium battery in which lithium acts as anode and cathode is solid manganese dioxide.

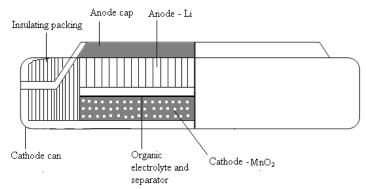
Anode: Lithium disc

Cathode: Manganese dioxide

Electrolyte: A solution of lithium halide in organic solvent *Separator:* Polypropylene impregnated with electrolyte

Cell voltage: 3.2Volts

Construction



During discharge lithium undergo oxidation liberating lithium ions. At cathode lithium ions reacts with manganese dioxide and forms an interstitial compound. During reduction reaction Mn⁴⁺ is reduced to Mn³⁺ and the reactions are as follow;

Reactions

At anode: Li \longrightarrow Li⁺ + e⁻

At cathode: $MnO_2 + Li^+ + e^- \longrightarrow LiMnO_2$ Overall reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

Applications

 $Li - MnO_2$ is used;

- As a long term memory backup
- In photoflash, Cameras, watches and calculators etc.

2. Construction, working and applications Li-ion battery

Anode: Lithiated carbon

Cathode: lithium metal oxide such as LiCoO₂, LiNiO₂

Electrolyte: Liquid electrolytes are solutions of a lithium salt (like LiPF₆, LiBF₄) in organic solvents, typically carbonates (like EC-ethylene carbonate, PC-propylene carbonate, DMC (dimethyl carbonate)

Separator: Microporous polyethylene or polypropylene separator film that employ a liquid electrolyte

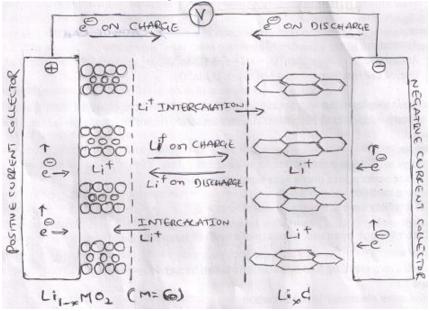
Construction and working

Lithium ion battery consists of a Cathode material typically a metal oxide with a layered structure, such as lithium cobalt oxide (LiCoO₂) and anode is a Lithiated carbon. The cathode and anode electrodes are electrically isolated by a microporous polyethylene or polypropylene separator film containing the liquid electrolyte. When the battery is charged and discharged, lithium ions are exchanged between the positive and negative electrodes. During charge/discharge process, lithium ions are inserted or extracted from interstitial space between atomic layers within the cathode and anode active materials and is known as *intercalation mechanism*.

Intercalation Processes

During intercalation reaction, the active materials (anode and cathode) operate by reversibly incorporating lithium ions, without undergoing a significant structural change. The positive material in a Li ion cell is a metal oxide, with both a layered or tunneled structure and the graphitic carbon negative materials have a layered structure similar to graphite.

Cell Notation: Li_xC, xLi⁺-C/ lithium salt in organic carbonate solvents carbonates /Li_{1-x}CoO₂, LiCoO₂



Reactions

At anode:
$$C + xLi^+ + xe^- \longleftrightarrow Li_xC$$
Discharge

Charge

At Cathode:
$$\text{LiCoO}_2 \longleftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$$

Discharge

Charge

Charge

Overall cell reaction: LiCoO₂ + C $Li_xC + Li_{1-x}CoO_2$ \leftrightarrow Discharge

Applications:

• In consumer electronics, such as cell phones, laptop computers

In military electronics, including radios, mine detectors and thermal weapons

Advantages:

Long cycle life

■ Wide operating temperature range (charge at -20°C to 60°C, discharge at -40°C to 65°C)

Long shelf life

Low self-discharge rate

High specific energy and energy density

FUEL CELLS

Fuel cell is a galvanic cell in which chemical energy of a fuel is converted into electrical energy by subjecting fuel to oxidation process, in presence of a suitable oxidizing agent. Any fuel cell consists of two electrodes and an electrolyte, separated by an ion exchange membrane. Here the fuel and oxidising agents are continuously supplied to the electrodes, at which electrochemical reactions take place producing current. The cells are capable of producing current as long as fuel and oxidizing agents are supplied and a general notation for fuel cells is presented below;

Fuel/electrode/electrolyte/electrode/oxidant

The combination of fuel and electrode constitute anode at which fuel undergo oxidation liberating electrons. The oxidant and electrode form cathode where oxidant consume electrons and undergo reduction.

Advantages: Fuel cells possess several advantages over conventional batteries;

- No moving parts and easy elimination of water formed
- Silent operation
- Does not form harmful products
- Charging not required

Disadvantages:

- Fuel (H₂ and CH₃OH) and oxidant (O₂) need to be stored in tanks under high pressure
- Electrodes used are costly
- Works as long as fuel and oxidant supplied

Difference between Fuel cells and Batteries

Fuel cells **Batteries** Fuel and oxidant are not stored in the fuel cell the active materials are stored in the battery No self-discharge problem Undergo self-discharge Ecofriendly in nature, no harmful products produce harmful products, not ecofriendly

Classification based on working temperature Electrodes used are very costly Example; $H_2 - O_2$ & $CH_3OH - O_2$ cells

Based on reversibility of reaction relatively cheaper electrodes employed Example; Zn –MnO₂, Zn – air, Ni – Cd cells

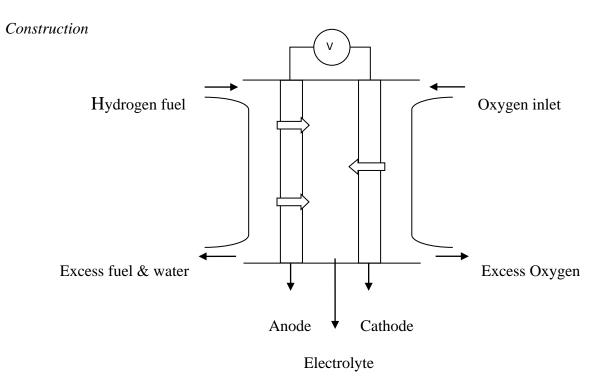
Classification of fuel cells

Fuel cells have been classified into three categories based on the temperature at which they are operated;

- (i) Low temperature fuel cells: This category of fuel cells make use of aqueous electrolytes and operate at temperature less than 100°C. Example: H₂-O₂ Fuel cell, CH₃OH-O₂ Fuel cell
- (ii) Moderate temperature fuel cells: These fuel cells operate at a temperature of 200°C and use molten salts as electrolytes. Example: Phosphoric acid fuel cell
- (iii) High temperature fuel cells: They work up to 600°C. Example Molten carbonate fuel cell
- (iii) Very high temperature fuel cells: In this type of fuel cells ceramic electrolytes are used and they operate at 1000°C Example: Solid oxide fuel cell

1. SOLID OXIDE FUEL CELL (SOFC)

SOFC is an extremely efficient fuel cell in which chemical fuels directly converted to electrical power.



Anode: A porous layer, mixture of Nickel and YSZ (Yettria stabilized Zirconia) known as 'cermet' is the anode.

Cathode: The mixture of LSM (Lanthanum Strontium Manganite) and YSZ powders, roughly in the ratio 50/50 forms the cathode layer at the electrolyte surface.

Electrolyte: Solid oxide electrolyte made of yttria-stabilized Zirconia (YSZ), acts as a conductor of oxide ions.

Connector: An inert and impervious conducting material is used to interconnect anode on one side and the cathode on the other. Lanthanum chromite has been used interconnecting material in SOFCs, operating near 1000°C.

Working: In SOFC a solid electrolyte made up of ZrO_2 (Zirconia) and 10mole% of Y_2O_3 (Yettria) becomes an ionic conductor at $600^{0}C$ - $1000^{0}C$ temperature range. The conduction takes place by the migration of oxygen ions (O^{2-}) from cathode to anode through molten electrolyte, where it reacts with hydrogen ions to form water.

Reactions: The electrochemical reactions are given below;

at anode; $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

 $CO + O^{2-} \rightarrow CO_2 + 2e^-$ (in case of reformed fuel)

at cathode; ${}^{1}\!\!/_{2}O_{2} + 2e^{-} \rightarrow O^{2-}$ net reaction; $H_{2} + {}^{1}\!\!/_{2}O_{2} \rightarrow H_{2}O$

Advantages

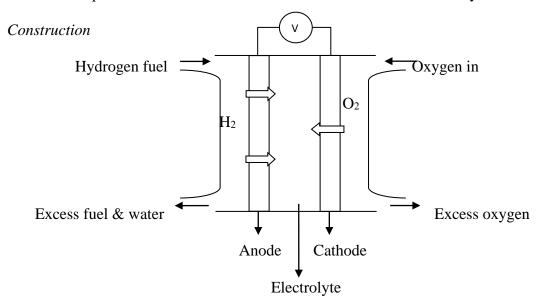
- Avoids use of expensive catalysts
- High tolerance to impurities
- No liquids in the cell

Disadvantages

- Relatively less efficient
- Difficulties in the fabrication of cathode materials

2. PHOSPHARIC ACID FUEL CELL (PAFC)

It was developed in the mid-1960 and the field test was started from the year 1970.



a. Electrolyte: The electrolyte is an inorganic acid, concentrated phosphoric acid (100%) a proton conductor is absorbed into a solid matrix of silicon carbide. (Since the specific conductivity (κ) of H₃PO₄ is quite low at temperature less than 100°C, 100% H₃PO₄ is used as electrolyte at 200°C.)

b. Electrodes: PAFCs employ gas diffusion electrodes. Both anode and cathode are carbon bonded with PTFE (about 30–50 wt %) form an electrode-support structure, where Pt supported on carbon acts as the electro-catalyst.

In the cell, the carbon is used to;

- Disperse the Pt catalyst for its better utilization
- Provide micropores in the electrode for maximum interaction of diffused gas with catalyst
- Increase the electrical conductivity of the catalyst

c. Working: The concentrated Phosphoric acid undergo electrolysis at high temperature around 150°C, as it is poor conductor at lower temperature. At anode pure hydrogen (if sulphur present, poisons Pt catalyst) acts as fuel and undergo catalytic oxidation forming hydrogen ions and electrons. Oxygen gas at cathode diffuses through the electrolyte and combines with protons to form water, the reactions are given below;

d. Reactions

at anode: $2H_2 \rightarrow 4H^+ \rightarrow 4e^$ at cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Net reaction: $2H_2 + O_2 \rightarrow 2H_2O$

Advantages

- PAFCs can tolerate a CO concentration of about 1.5 percent, which offers more option for the selection suitable fuel
- It allows the use of impure hydrogen as fuel
- The expelled water can be converted to steam, for air and water heating

Disadvantages

- At lower temperatures phosphoric acid is a poor ionic conductor
- Pt catalyst severely poisoned by CO