

ENERGY STORAGE DEVICES

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7. Oxygen Sensor
8. Super Capacitors
9. Ragone plot

Unit III Energy storage devices

Battery is an arrangement of two or more galvanic cells connected in a parallel or series to increase voltage or Battery is an arrangement of two or more cells usually arranged in parallel or series to produce necessary voltage or current or both.

The battery was the first practical source of electrical energy developed in man's search for portable power sources. Although many other technologies have been developed for supplying electrical power, the battery is the most widely used source of electrical power when portability is the prime requisite.

Batteries are used in hearing aids, flash lights, clocks, emergency lighting, tape recorders, toys, calculators, telephone systems, electric bells, space vehicles, military applications etc.

Battery technology historically considered electrochemical, combines the activities of the chemist, the chemical engineer, the material specialist, the electrical engineer, the environmental engineer and instrumental analyst. The individual view points of all these, cooperate to serve the diversified needs and desires of industries, as well as our daily lives in the electronic and space age.

Important requirements of Battery components

- The electrode reaction must be rapid. For secondary batteries charging must be fast
- The two electrodes must have sufficiently different equilibrium half potentials, so that useful cell voltage can be obtained.
- The active components of the cell should only react when the external circuit is closed. There should be no self-discharge.
- The battery should have as large power and energy density as possible
- The cell components should be cheap and easily available. They should not be poisonous and should be disposable without any environmental pollution

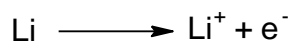
Components of a battery

The essential components of battery are as follows.

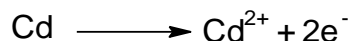
1. Anode or negative electrode:

It is a negative electrode at which oxidation of the species occur. It releases electrons to the external circuit by undergoing oxidation during electrochemical reaction.

Example: Lithium metal in Li-MnO₂ battery.



Cadmium metal in nickel cadmium battery.

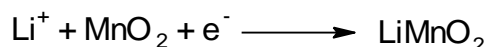


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2. Cathode or Positive electrode:

It is a positive electrode at which reduction of the species occur. It accepts electrons from the external circuit and reduces active species.

Example: MnO_2 is used as cathode in Li- MnO_2 battery.



3. Electrolyte:

It is an active mass in both the anode and cathode compartments. A solution of an acid, alkali or salt having ionic conductivity is commonly used as electrolyte. Solid electrolytes with appreciable ionic conductivity at the operating temperature of the cell are also used.

Example: KOH is used as an electrolyte in nickel cadmium battery.

H_2SO_4 is used as an electrolyte in lead acid battery.

4. Separator:

It separates the anode and cathode compartments to prevent internal short circuit. It is permeable to the electrolyte and maintains desired ionic conductivity. It is electronically an insulator but ionically conductor. The main function of a separator is to transport ions from the anode compartment to cathode compartment and vice versa.

Example: Micro porous polypropylene or polyethylene, cellophane, nafion membrane

Apart from anode, cathode, electrolyte and separator, other components are

Container or battery housing:

Entire battery is enclosed with a insulating material like wood or paper or plastic to isolate battery materials from external environment.

Current collector:

A conducting backbone of a electrode in a battery is current collector. It is made up of a material with high electrical conductance and high surface area to accommodate more amount of active species on its surface.

Example: Al and Cu current collectors in Li-ion battery

Nickel coated steel mesh in nickel-cadmium battery

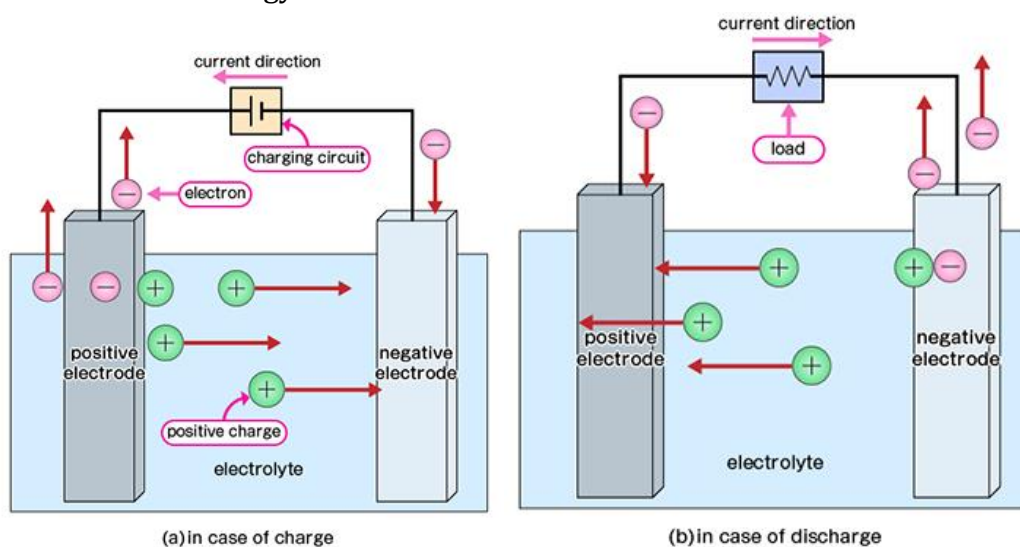
Working of a battery:

Discharging:

During discharge, a battery delivers power. Oxidation takes place at the anode and reduction takes place at the cathode. The reaction is a spontaneous reaction. Chemical energy is converted into electrical energy.

Charging:

During charging, reverse reactions take place. The reverse reactions are non-spontaneous reactions. The battery is connected to an external dc power supply. Electrical energy is converted in to chemical energy.



Based on working, two types of batteries:

Primary battery

- Electroactive material cannot be regenerated
- Discarded after electroactive species is consumed
- Galvanic cell
- Dry cell, Li-MnO₂

Secondary battery

- Electroactive material can be regenerated
- Can be used several times
- Galvanic as well as electrolytic cell
- Storage battery
- Li-ion, Pb-acid, Ni-Cd

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Battery Characteristics

1. Voltage: The voltage available from a battery depends upon the EMF of the cell. The EMF of the cell depends on change in free energy of overall cell reaction.

According Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

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

Where Q is the reaction quotient. It is also evident from the equation, EMF of the cell and also the voltage available from the battery is depending on standard electrode potential difference between the cathode and anode, temperature and the extent of the cell reaction.

If the difference in the standard electrode potential is more, higher is the EMF of the cell.

As the temperature increases the EMF of the cell decreases.

As the value of Q increases, the EMF of the cell decreases.

To derive a maximum voltage from the cell

- ✓ The electrode potential difference between cathode and anode must be high
- ✓ Polarization and over potential must be minimum
- ✓ Internal resistance must be low

2. Current: It is the measure of the rate at which battery is discharging. To construct efficient battery large quantity of active materials must be maintained for rapid electron transfer without any excessive voltage penalty. More the electro active materials packed in the cell more is the current generated.

It depends on conductivity of electrolyte. With increase in electrolyte concentration, conductivity of electrolyte increases. The resistance decreases and hence current increases.

It also depends upon distance between the electrodes. By increasing the distance between the electrodes, the resistance of the electrolyte increases and hence current increases.

3. Capacity :

The capacity is the charge or amount of electricity that may be obtained from the battery and is given in ampere hours (Ah). Capacity depends on size of the battery and is given by Faraday's relation

$$C = \frac{wnF}{M}$$

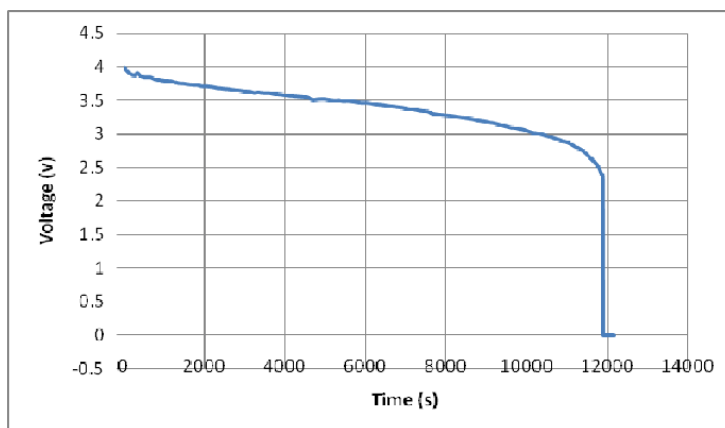
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where w is the mass and M is the molar mass of active material.

The amount of the active material actually consumed during discharge determines the capacity of the battery. The capacity also depends on the discharge conditions. It is measured by finding the time ' t ' taken for the battery to reach a minimum voltage for a fixed current discharge (i amperes). The cell is said to be dead at minimum voltage.

A plot of time against voltage at a fixed current discharge is shown in the figure.

The length of the flat portion of the curve is a measure of the capacity of the battery; longer the flat portion better is the capacity.



The capacity $C = it$. Where t is the time required by the battery during discharge of fixed current i amperes to reach a value E_{\min} . Flatter and longer the curve better is the capacity.

4. Power density

It is the power per unit weight of the battery. It is the ratio of the power available from a battery to its mass (W/kg) or volume (W/L)

$$\text{Power density} = \frac{\text{Power available from the battery}}{\text{Mass of the battery}}$$

$$\text{Power density} = \frac{i \times E_{\text{cell}}}{W}$$

Where W is mass of the battery, i and E_{cell} are current and EMF generated in the cell.

Power density is expressed in Wkg^{-1}

During discharge power density decreases.

5. Energy density

It is the ratio of energy available from the battery to its mass (or volume)

$$\text{Energy density} = \frac{\text{Energy available from the battery}}{\text{Mass of the battery}}$$

$$\text{Energy density} = \frac{i \times E_{\text{cell}}}{W} \times t$$

Where W is mass of the battery, i and E_{cell} are current and EMF generated in the cell, t is time.

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The unit of energy density is Whkg^{-1}

A cell with a good energy density is preferred.

6. Energy efficiency:

When secondary batteries are used for energy storage on large scale, the energy efficiency becomes important.

The energy efficiency of secondary battery is given by

$$\text{Percentage of Energy efficiency} = \frac{\text{Energy released on discharge}}{\text{Energy required for charging}} \times 100$$

- Higher the energy efficiency better is the battery
- Depends on efficiency of electrode reactions

7. Cycle life

Primary batteries are designed for single discharge, but a secondary battery is rechargeable.

The cycle life is the number of charge/discharge cycles that are possible before failure occurs.

Why batteries have limited cycle life?

Reasons for failure to achieve high cycle life is,

1. Corrosion at contact points.
2. Shedding of active material from the plates.[Loss of electro active materials from the electrode due to rapid charging conditions]
3. Shorting between electrodes due to irregular crystal growth and change in morphology.

8. Shelf life

Shelf life is the maximum time for which a given battery can be stored without self-discharge or corrosion or loss of performance.

Batteries need to be stored for longer time without self-discharge. Shelf life is affected by self discharge. Self discharge occurs when there is reaction between the anode and cathode active material or corrosion of current collectors. OR

The duration of storage under specified condition at the end of which a cell or a battery retains the ability to give specified performance is called the shelf life.

Batteries need to be stored for longer time without self-discharge. Self discharge occurs when there is reaction between the anode and cathode active material or corrosion of current collectors.

9. Electricity storage density

It is the amount of electricity per unit weight which the storer can hold. In other words, it is the capacity per unit mass of the battery.

The weight of the battery includes, weight of electrodes, electrolyte, terminals, case and current collectors. To get high electricity storage density, weight of all the elements should be minimum.

For example, 7 g of lithium is required at anode to give 96500 C of charge where as for the same charge 65 g of zinc is required.

10. Tolerance to service conditions

The battery has to be tolerant to different service conditions such as variation in temperature, vibration and shock

Modern batteries

Zinc-air battery

Zinc-air battery is a type of metal-air batteries, which uses oxygen directly from the atmosphere to produce electrochemical energy. Oxygen diffused into the cell and is used as the cathode reactant. The air cathode catalytically promotes the reaction of oxygen with an alkaline electrolyte and is not consumed or changed during discharge. As the cathode can be very compact, high energy densities are achieved.

Construction:

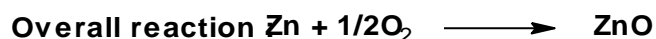
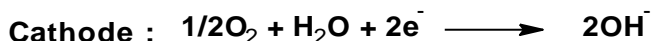
Anode : Loose powdered zinc with an aqueous alkaline electrolyte and gelling agent (to immobilize the composite and ensure adequate contact with zinc granules).

Cathode : Amorphous carbon (graphite) blended with MnO_2 (catalyst) with a wet proofing agent coated on nickel wire mesh support and an outer layer of air permeable Teflon layer. Air access holes on the cathode provide pathway for O_2 to enter the battery

Electrolyte : 30 % KOH

Separator : Polypropylene membrane soaked in electrolyte.

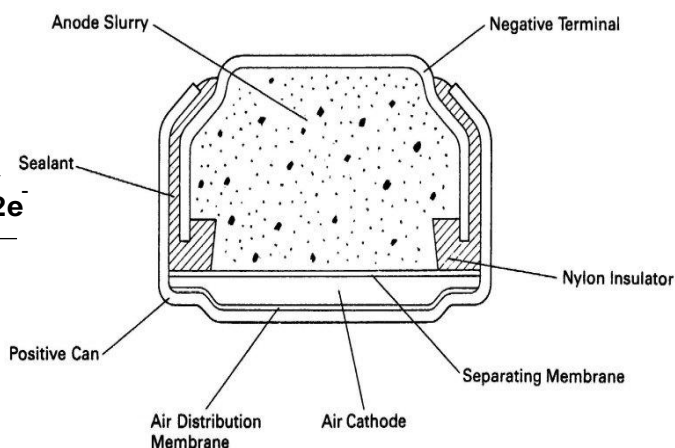
Working :



The cell produces an open circuit potential of 1.4 V.

Advantages :

1. High energy density (1000 Whr/kg) : Air does not contribute to the mass of the battery
2. Long shelf life : It can be kept sealed



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3. No ecological problems
4. Low cost

Disadvantages :

1. Limited power output
2. The battery is exposed to atmosphere, therefore CO_2 may enter into the battery. It reacts with KOH forms K_2CO_3 precipitate, which will reduce the efficiency of the battery.

Applications :

1. Used as power source in hearing aids
2. Used in various medical devices
3. Large zinc-air batteries are used in rail-road signaling
4. In voice transmitters

Lithium batteries

The reasons for the selection of lithium metal as anode is,

1. Lithium is light weight metal with good electrical conductivity.
2. It has very high negative standard electrode potential of -3.05 V . It can be coupled with other electrodes with high standard electrode potential to get high voltage (about 4 V)
3. The electrochemical equivalence of lithium is high (7 g of Lithium can give 1F of charge)

Advantages :

1. High Voltage up to 4 V depending on the cathode material. This is because of the very negative electrode potential of Li/Li^+ .
2. High energy density – Lightest metal
3. High tolerance to service conditions (-40°C to 70°C)
4. High electricity storage density
5. Flat discharge characteristics
6. Low self discharge rate

Disadvantages :

1. Safety concerns due to high reactivity of Lithium metal.
2. Poor cycle life – due to dendrite formation.
3. Transportation limit

Classification of Lithium batteries

Primary battery : It is not rechargeable. E.g. : Li-MnO_2 battery

Secondary battery : It is rechargeable. E.g.: Li-ion battery

Pure lithium is highly reactive. It reacts vigorously with water to form lithium hydroxide and hydrogen gas. Thus non-aqueous electrolytes are typically used and a sealed container rigidly excludes moisture from the battery pack.

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Lithium – ion battery

A lithium battery is a member of a family of rechargeable battery types in which lithium ions move from the negative electrode to positive electrode during discharge and back when charging. Lithium ion batteries use an intercalated lithium compound as an electrode material, compared to the metallic lithium used in a non-rechargeable lithium battery. The electrolyte which allows for ionic movement, and the two electrodes are the constituent components of a lithium ion cell.

Construction:

Anode : Lithiated -Carbon (Graphite) coated on copper current collector

Cathode: Lithiated transition metal oxide coated on aluminium current collector.

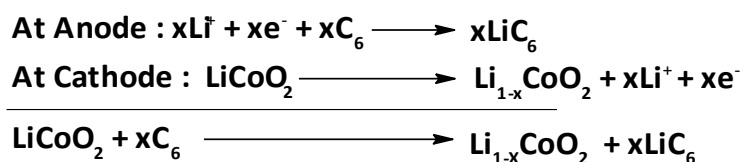
E.g. : Lithium cobalt oxide.

Electrolyte: The electrolyte is typically a mixture of organic carbonate solvents such as ethylene carbonate or diethyl carbonate containing lithium salts like LiPF_6 , LiClO_4

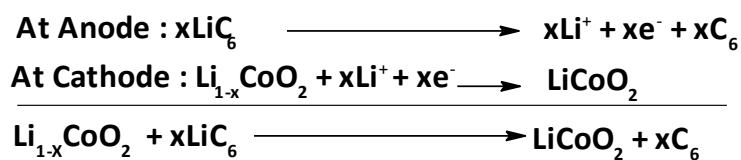
Separator: It is a very thin sheet of micro perforated polypropylene membrane.

Working :

During Charging :



During Discharging :

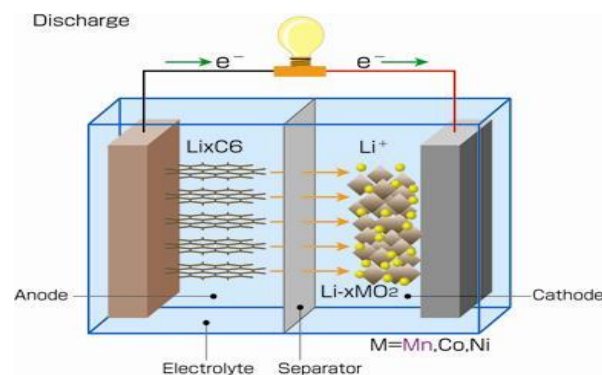


Advantages :

1. Lighter than other rechargeable batteries for a given capacity.
2. Li-ion battery delivers a high open-circuit voltage 3.7 V
3. Low self-discharge rate
4. Do not suffer from battery memory effect
5. Good cycle life as the problem of dendrite formation is eliminated (at no point, neither charging nor discharging, Lithium metal is formed)

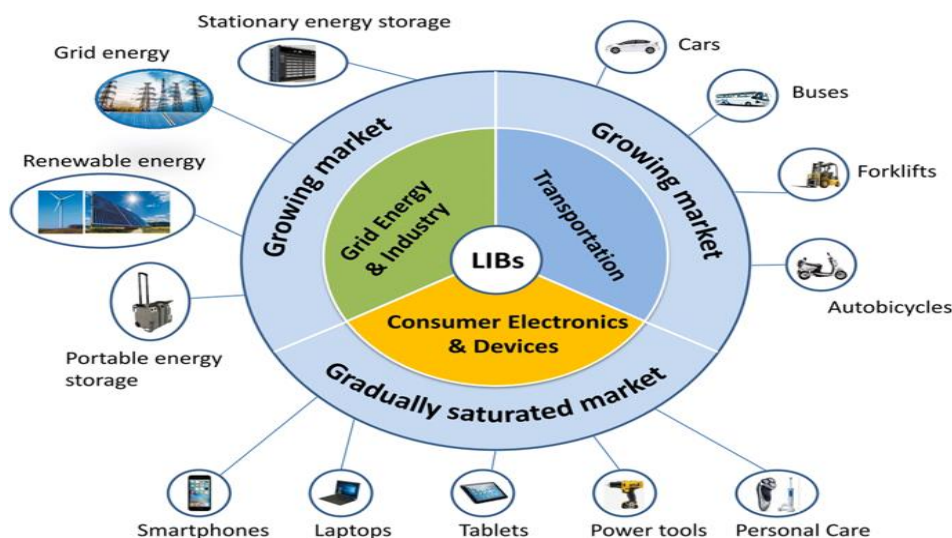
Disadvantages :

1. Rising internal resistance with cycling and age
2. Safety concerns if overheated or overcharged



Unit III Energy storage devices

Applications :



Reserve Batteries

A battery in which one of the key component is kept separated from the rest of the battery to achieve long shelf life is called reserve battery. Usually the electrolyte is the component that is isolated. When one of the key components of the cell is separated from the rest of the cell, chemical reaction between the cell components (self discharge) is prevented and hence reserve battery has unlimited shelf life.

Classification of Reserve Batteries

1. Water-activated batteries : Activation by fresh or sear water
2. Electrolyte-activated batteries : Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.
3. Gas-activated batteries : Activation by introducing a gas into the cell
4. Heat -activated batteries : A solid salt electrolyte is heated to molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries.

Magnesium – water activated battery

Construction:

Anode (Negative Plate): Magnesium sheet.

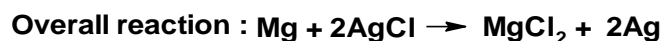
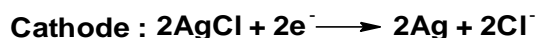
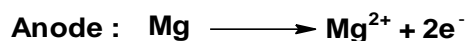
Cathode (Positive Plate): Silver chloride sheets covered with silver on the surface by reduction to make conducting electrode surface.

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Separators: Woven or nonwoven fabric, absorbent, nonconductive material is utilized for the dual purpose of separating the electrodes and absorbing the electrolyte.

Electrolyte: water or sea water

Working :



Advantages:

1. Reliable
2. Safe
3. Instantaneous activation
4. Long shelf life
5. Light weight as electrolyte need not be stored in the battery

Disadvantages:

1. High discharge after activation
2. Once activated must be replaced

Applications:

Sonobuoys, Electric torpedoes, Weather balloons, Air-sea rescue equipment, Pyrotechnic devices, Marine markers and Emergency lights.

Fuel Cells

The conventional method of utilizing the chemical energy of a fuel involves several steps and can be depicted as follows :

Chemical energy \rightarrow Thermal energy \rightarrow Mechanical energy \rightarrow Electrical energy

Thermal energy liberated during the combustion of a fuel is used to convert water into steam. the steam is used to drive turbine that drives the generator to produce electrical energy. There is a loss of energy in every step and only a maximum of 40% energy of the fuel is converted into electricity. But in galvanic cell chemical energy is directly converted into electrical energy and the efficiency of conversion is very high.

A fuel cell is a galvanic cell which converts chemical energy of a fuel oxidant system directly into electrical energy by means of redox reaction or electrochemical reactions.

A fuel cell consists of the following arrangement

Fuel | Electrode | Electrolyte | Electrode | Oxidant

Anode : Fuel \rightarrow Oxidation product $+ \text{ne}^{-}$

Cathode : Oxidant $+ \text{ne}^{-} \rightarrow$ Reduction products

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Advantages :

1. High power efficiency. (Theoretical efficiency is 100%, but actually it is about 50 - 80%)
2. Eco-friendly - products of the overall reactions are not toxic.
3. Silent operation.

Disadvantages :

1. Cost of the power is high as a result of the cost of the electrodes.
2. Power output is moderate.
3. Fuels are in the form of gases and oxygen need to be stored in tanks under high pressure.

Applications:

1. Used as auxiliary power generators in space vehicles
2. They are used in vehicles
3. Large scale power generation

How is fuel cell different from a battery?

| Battery | Fuel cell |
|--|---|
| These are the energy storage devices | These are energy conversion devices |
| Secondary batteries are rechargeable | Fuel cells are not chargeable |
| The reactants and products form integral part of the batteries | In fuel cells, there is a continuous supply of fuel and oxidant |
| Products remain in the cell | Products are continuously removed from the cell |
| May pose pollution problem | Eco friendly |

Efficiency of a fuel cell

Thermodynamic efficiency is given by the ratio of work output to heat input

Work output is Gibb's free energy ; heat input is enthalpy change of the cell reaction

Gibb's free energy, ΔG - Measure of the electrical work done

Enthalpy change, ΔH - Measure of the heat released during the reaction

$$\text{Efficiency } \eta = \frac{\Delta G}{\Delta H} \times 100$$

Classification of fuel cells

Based on the type of an electrolyte used in the fuel cells can be classified as follows :

1. H_2 - O_2 Alkaline fuel cells
2. Direct-methanol fuel cells (DMFCs) or CH_3OH - O_2 Polymer electrolyte membrane fuel cells
3. CO - O_2 Solid oxide fuel cells
4. Phosphoric acid fuel cells
5. Carbonate fuel cells

1. H₂-O₂ Alkaline fuel cells

Alkaline fuel cells use an aqueous solution of KOH as electrolyte due to the following reasons:

1. Oxygen reduction is more rapid in alkaline electrolytes than in acid electrolytes
2. The use of non noble metal electro-catalyst is feasible.

Construction :

Anode : Porous carbon impregnated with Pt/Pd catalyst

Cathode : Porous carbon impregnated with Pt/Ag catalyst

Electrolyte : 30-45 % KOH(warm)

Fuel : Hydrogen gas

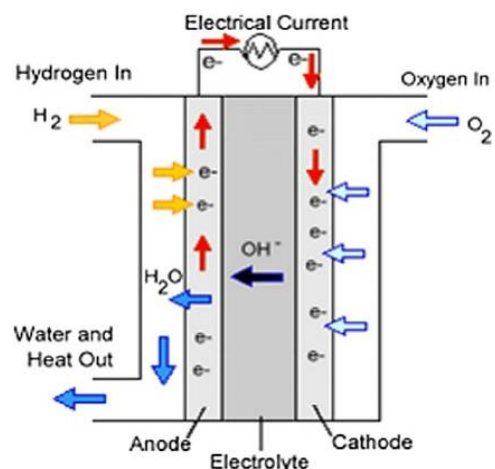
Oxidant : Oxygen gas

Working : At Anode : $\text{H}_2 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + 2\text{e}^-$

At Cathode : $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$

Over all reaction : $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$

$$\text{Emf} = 1.23 \text{ V}$$



- H₂ gas diffuses through anode, gets adsorbed on the electrode surface, reacts with OH⁻ to form water
- At cathode O₂ diffuses through electrode, is adsorbed and reduced to OH⁻
- Product is water which dilutes the KOH
- Cell operates at 100 °C, so that water from KOH escapes as steam
- The water was used by astronauts for drinking on Apollo spacecraft

Advantages:

1. Operates at low temperature
2. Have minimum corrosion
3. Alkali is used as electrolyte hence non noble metal catalyst can be used

Disadvantages:

1. In this type of cell reactants must be free from CO₂, because the alkali reacts with CO₂ to form carbonates which would block the pores of electrodes and reduce efficiency of the cells.
2. Having liquid electrolytes, introducing handling problems.

2. Direct-methanol fuel cells (DMFCs) or CH₃OH-O₂ Polymer electrolyte membrane fuel cells

Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel. Their main advantage is the ease of transport of methanol and reasonably stable liquid at all environmental conditions.

Whilst the thermodynamic theoretical energy conversion efficiency of a DMFC is 97 %; the currently achievable energy conversion efficiency for operational cells attains 30 % - 40 %. Polymer membrane or proton exchange membrane is used as electrolyte. They are known as proton exchange membrane fuel cells. They are low temperature fuel cells (60-90 °C), have low weight and volume.

Construction:

Anode: Porous carbon electrode containing platinum

Cathode : Porous carbon electrode containing platinum

Fuel: Solution of CH₃OH

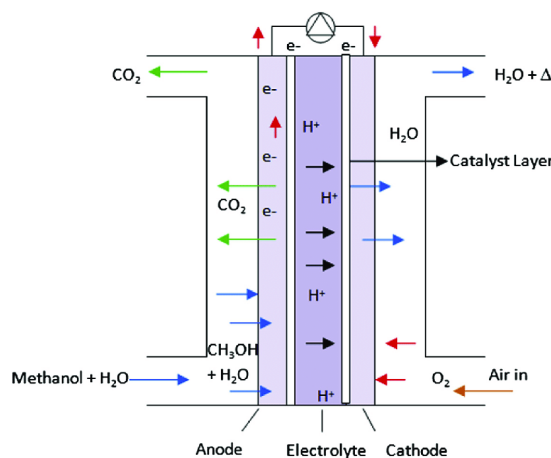
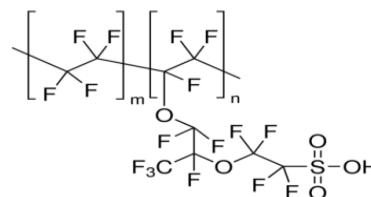
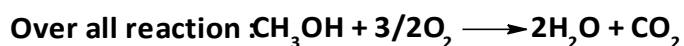
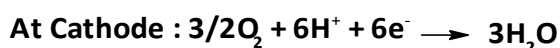
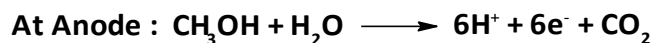
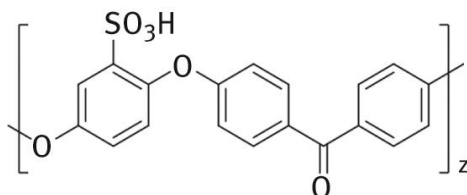
Oxidant: Oxygen gas

Electrolyte: proton conducting polymer membrane

They use a polymer membrane as its electrolyte. This membrane is an electronic insulator but an excellent conductor of H⁺ ions. E.g. : Nafion

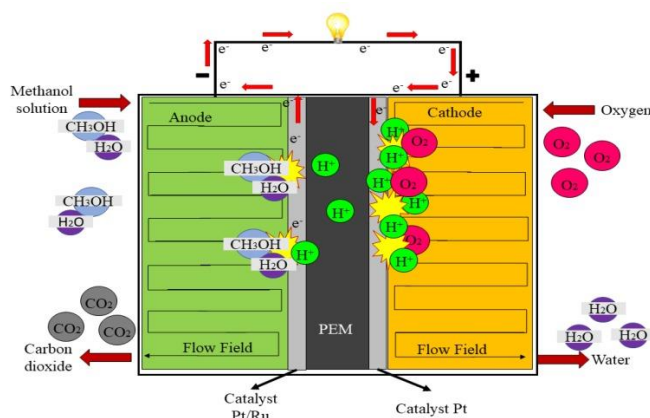
Nafion: This polymer consists of fluorocarbon backbone (–CF₂–CF₂–) similar to teflon to which sulphonic acid groups are attached. The protons on sulphonic acid group are free to migrate through the hydrated membrane.

- For DMFC Nafion not suitable as it has high permeability for CH₃OH, hence methanol crossover happens
- Methanol crossover - CH₃OH diffuses through the membrane to cathode without undergoing oxidation at anode resulting in low performance
- New membranes are being used - Poly electrolyte membranes e.g., SPEEK - sulphonated poly(ether ether ketone)



$$E_{mf} = 1.21V$$

- A aqueous solution of methanol is fed at the anode
- Common operating temperatures are in the range 60 - 90 °C
- Oxidation of methanol on a catalyst layer takes place to form carbon dioxide , protons and electrons
- Protons (H^+) are transported across the proton exchange membrane – to the cathode where they react with oxygen to produce water
- Water is consumed at the anode and produced at the cathode
- Electrons are forced to travel through an external circuit from anode to cathode, providing power to connected devices



- Water management is very important for Proton exchange membrane fuel cells
- Temperature has to be maintained constant (60-90 °C)
- Polymer membrane must remain hydrated to maintain H^+ conductivity
- Water produced from the reaction must be removed from the cathode
- High temperatures
 - may dehydrate the polymer so H^+ conductivity cannot take place
 - the polymer may degrade and crack resulting in short circuit
- Low temperatures
 - will result in flooding of the cell thereby reducing efficiency of the cell
 - a higher catalyst loading will be required

Advantages:

1. High energy density : Due to the low weight of the polymer.
2. Long life : Low temperature operation allows them to start quickly and results in less wear on system components, resulting in better durability.
3. No free corrosive liquid in the cell

Disadvantages:

1. Noble metal catalysts have to be used (Pt) and electrolyte is expensive so cell cost is high
2. CO, if present, poisons the Pt catalyst, hence pure reactants should be used
3. Management of carbon dioxide created at the anode and water management pose problems

Applications :

1. Used in military applications - since they have low noise and thermal signatures and no toxic effluent.

3. CO-O₂ Solid oxide fuel cells (SOFC)

Solid oxide fuel cells are a class of fuel cells characterized by the use of a solid oxide material as the electrolyte. The electrolyte is a ceramic material yttria stabilized zirconia (YSZ) i.e. zirconium oxide doped with yttrium oxide.

SOFCs use a solid oxide electrolyte to conduct negative oxygen ions from the cathode to the anode. The electrochemical oxidation of the hydrogen, carbon monoxide or other organic intermediates by oxygen ions thus occurs on the anode side.

This is high temperature fuel cell operates in between 650 - 1000 °C.

Construction:

Anode : Ni-ZrO₂ or Co-ZrO₂

Cathode : Porous Sr doped with LaMnO₃

Fuel: CO

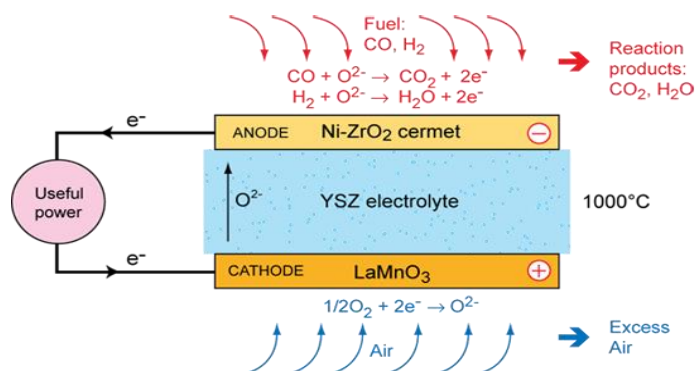
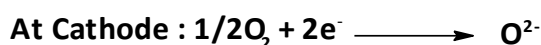
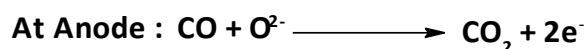
Oxidant : O₂

Electrolyte : Solid nonporous metal oxide usually ZrO₂ doped with Y₂O₃ which is commonly called yttria stabilized zirconia (YSZ). When ZrO₂ is doped with Y₂O₃, oxide ion (O²⁻) vacancies are created.

O²⁻ ions can move through the solid oxide membrane.

YSZ shows sufficient ionic conductivity, chemical stability and mechanical strength at high temperatures.

Working :



- Oxygen is supplied at the cathode
- Oxygen reacts with the incoming electrons from the external circuit to form oxide ions(O²⁻)

- O^{2-} travel through the electrolyte which has oxide ion vacancies and reach the anode
- At the anode the O^{2-} react with the CO to form CO_2 , liberating electrons
- Electrons flow from anode to cathode through the external circuit thereby generating power

Advantages:

1. No expensive catalyst required since works at a high temp.
2. CO can be used as a fuel - CO is not used in cells where Pt is used as catalyst as CO poisons the catalyst or in cells which use alkali as electrolyte as CO will form CO_2 which reacts with the alkali and forms carbonates which reduce efficiency of the cell
3. Their high temperatures make them particularly efficient for Combined Heat and Power (CHP) systems, as waste heat can be put to good use for heating and cooling.

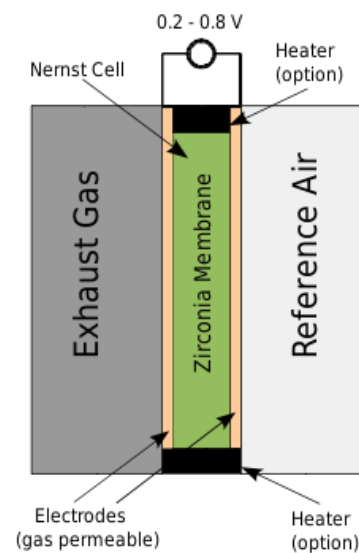
Disadvantages:

1. Very slow start up as high temperature has to be reached.
2. High temperature enhances the corrosion of the components
3. Few materials can operate at high temperature and remains stable at high temperature

Oxygen Sensor

An Oxygen sensor or lambda sensor is an electronic device that measures the proportion of O_2 in the gas or liquid being analyzed.

A gasoline engine burns gasoline in the presence of oxygen. It turns out that there is a particular ratio of air and gasoline that is "perfect," and that ratio is 14.7:1 (different fuels have different perfect ratios - the ratio depends on the amount of hydrogen and carbon found in a given amount of fuel). If there is less air than this perfect ratio, then there will be fuel left over after combustion. This is called a rich mixture. Rich mixtures are bad because the unburned fuel creates pollution. If there is more air than this perfect ratio, then there is excess oxygen. This is called a lean mixture. A lean mixture tends to produce more nitrogen-oxide pollutants, and, in some cases, it can cause poor performance and even engine damage.



The oxygen sensor is positioned in the exhaust pipe and can detect rich and lean mixtures. The Oxygen sensor detects the amount of oxygen in the exhaust gas and sends a signal to the engine control unit which adjusts the air fuel mixture to the optimal level. Too much oxygen in the

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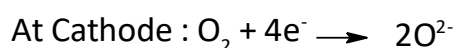
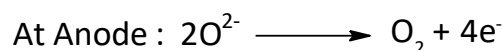
exhaust gas indicates a lean mixture, which can cause performance problems, including misfires. Too little oxygen indicates a rich mixture, which wastes fuel and results in excess exhaust emissions.

1. An O₂ sensor is actually a galvanic cell. The zirconium dioxide or zirconia lambda sensor is based on a solid-state electrochemical fuel cell. The sensor contains two platinum electrodes with an electrolyte between them. ZrO₂ doped with some Y₂O₃ is the electrolyte used. Due to doping some oxygen vacancies are created in the crystal lattice. The mobility of O₂⁻ ions is greatly enhanced and the conductivity is due to oxygen ions.

2. Cell voltage is given by

$$E_{\text{cell}} = \frac{2.303RT}{4F} \log \frac{P_1}{P_2}$$

Where P₁ and P₂ are the partial pressure of O₂ in reference air and exhaust gas respectively.



3. Its two electrodes provide an output voltage corresponding to the quantity of oxygen in the exhaust relative to that in the atmosphere.

4. An output voltage of 0.2 V represents a "lean mixture" of fuel and oxygen, where the amount of oxygen entering the cylinder is sufficient to fully oxidize the carbon monoxide (CO), produced in burning the air and fuel into carbon dioxide (CO₂).

5. An output voltage of 0.8 V represents a "rich mixture", one which is high in unburned fuel and low in remaining oxygen. The ideal set point is approximately 0.45 V. This is where the quantities of air and fuel are in the optimum ratio, such that the exhaust output contains minimal carbon monoxide.

1. O₂ sensors operate at a minimum temperature of 360 °C.
2. The O₂ sensor allows fuel management system to maintain the ideal air/fuel ratio across various engine operation conditions.
3. Leaded gasoline contaminates the O₂ sensors and catalytic convertors and results in failure of the sensor. Other reason for failure could be presence of impurities in gasoline.

Applications: Most common applications of O₂ sensors are:

1. Measure exhaust gas concentrations of O₂ in IC engines
2. Divers use to measure partial pressure of O₂ in their breathing gas
3. Scientists use as probes to measure respiration or production of O₂
4. In O₂ analyzers used in medical applications such as anesthesia monitors, respirators etc.

Super Capacitors

The supercapacitor, also known as ultracapacitor or double-layer capacitor, differs from a regular capacitor in that it has very high capacitance. A capacitor stores energy by means of a static charge as opposed to an electrochemical reaction. Applying a voltage differential on the positive and negative plates charges the capacitor. This is similar to the buildup of electrical charge when walking on a carpet. Touching an object releases the energy through the finger.

A capacitor is a passive electronic component comprising a pair of conducting plates separated by a dielectric. Capacitors store electrical energy as electrostatic charge with equal quantities of positive and negative charges on opposite faces of the conducting plates resulting in a voltage difference between the faces. When the two faces are connected by an external load, current flows until complete charge balance is attained and the stored energy is released. The capacitor can then be retrieved to its charged state by applying voltage. Since the charge is stored physically without any chemical or phase changes, the process is highly reversible and the charge-discharge cycle can be repeated over and over again, virtually without limit. The quantity of charge (Q) stored in a capacitor is equal to the device voltage (V) times proportionality constant (C) called capacitance,

$$\text{i.e. } Q = CV \text{ ----- (1).}$$

In Eq. (1), capacitance C is in Farad, charge Q is in Coulomb and the voltage V is in Volt. In vacuum, the capacitance of such a capacitor is proportional to the area (A) of the conductors divided by the thickness (d) of the dielectric separating them as shown in Fig. 1,

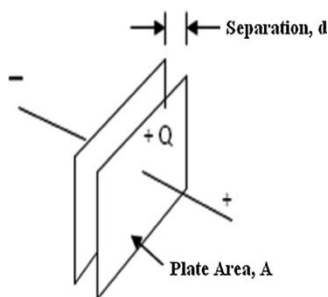


Fig. 1. Schematic sketch of a parallel-plate capacitor.

$$C = \frac{\epsilon_0 A}{d} \text{ -----(2)}$$

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In Eq. (2), proportionality constant $\epsilon_0 = 8.9 \times 10^{-12} \text{ Fm}^{-1}$ is the permittivity of the free space or vacuum. With the dielectric material of relative permittivity (ϵ_r), which increases the energy stored in the device, the capacitance (C) is then expressed as:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad \text{-----(3)}$$

On substituting Eq. (3) in Eq. (1), we get,

$$Q = \frac{\epsilon_r \epsilon_0 A}{d} V \quad \text{-----(4)}$$

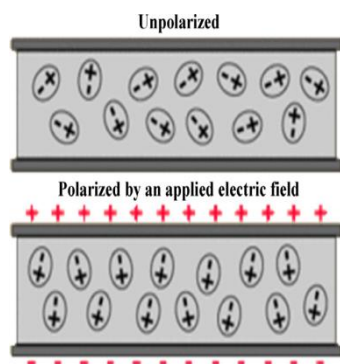


Fig. 2. A dielectric medium showing the orientation of charged particles creating polarization effects.

Electrical double-layer capacitor:

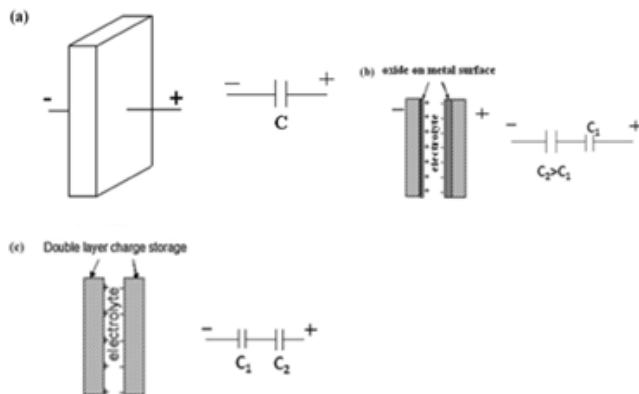


Fig. 3. Schematic sketches for a) Electrostatic, b) Electrolytic and c) Electrochemical capacitors

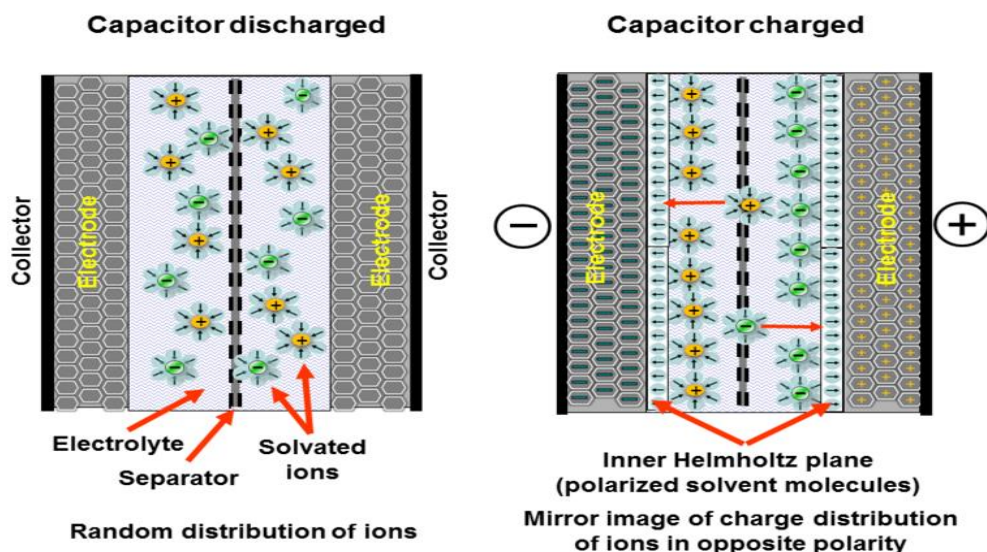


Fig. 4. Schematic sketch of an electrical double-layer capacitor

Electrical double-layer capacitor: It has long been accepted that an electrical double-layer exists at the electrode/electrolyte interface that governs adsorption phenomena and influences charge transfer reaction rates. As shown in (Fig.3c), the electrical double-layer stretches to about a few Å and stores electrostatic energy like a capacitor. It is noteworthy that the existence of the electrical double-layer has always been inferred from indirect observations of related properties and quantities, but never directly probed. It was realized only recently that the energy stored per unit surface area is significant and becomes technologically attractive with the introduction of materials with high active-surface-areas, such as activated carbons. In the electrical double-layer, solvated ions are attracted to the solid surface by an equal but opposite charge in the solid as shown in Fig. 4. These two parallel regions of charge form the source of the term electrical double-layer where the charge separation as measured in molecular dimensions is less than 10^{-9} m. As the surface area of activated carbon is nearly $1000 \text{ m}^2 \text{ g}^{-1}$ of material, this creates a capacitor cell with very high specific capacitance of nearly 10^5 F kg^{-1} and the possibility of realizing devices rated at many thousands of Farad. Owing to their appreciably high capacitance, these capacitors are also referred to as **supercapacitors or ultracapacitors**.

Electrical-double layer capacitors (EDLCs):

These capacitors rely on carbon-based structures utilizing non-faradaic electrostatic charging of the electrical double-layer formed at the electrode–electrolyte interface and are hence termed as electrical-double-layer capacitors.

EDLCs store electrical energy at the electrolyte/carbon interface through reversible ion adsorption onto the carbon surface, thus charging the electrical double-layer through a non-faradaic contribution between an electronic conductor, namely the carbon, and a liquid ionic-

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conductor, namely the electrolyte. The few nano-meter thick electrical double-layers at the phase boundary between the electrode and electrolyte can be referred to as a nano-dielectric similar to a parallel-plate capacitor wherein the current collector of each electrode contacts high-surface-area-conductive carbon impregnated with an electrolyte. At the negative electrode, the negative charges received during charge by an external source are balanced by the positive charges of the electrolyte cations that accumulate on the surface and within the pores of the carbon particles. The counter electrode charges itself positively against the surrounding solution.

Because of the formation of the electrical double-layer at each electrode/electrolyte interface, a complete cell is formed by two capacitors in series and the overall capacitance (C_T) is expressed as:

$$\frac{1}{C_T} = \frac{1}{C_+} + \frac{1}{C_-} \text{ -----(7)}$$

In Eq. (7), C_+ is the capacitance of cathode/electrolyte interface and C_- is the capacitance of anode/electrolyte interface. In an ideal electrical-double-layer capacitor, only charge separation takes place at the electrode and there are no oxidation or reduction reactions. Accordingly, charge (Q) stored in such a capacitor is related to its capacitance (C) and voltage (V) as: $Q = CV$. Consequently, the capacitance is voltage independent but does depend on electrode surface area, the double-layer thickness and dielectric constant of the electrolyte. Traditionally, activated carbons have been used in EDLCs. But conducting carbons with graphitic structure also include template and carbide-derived carbons, nanotubes, nanohorns, onions (multi shell fullerenes), polyhedral particles, carbon blacks and graphene.

Electrochemical capacitors have limited energy density but are known to exhibit high power densities. Accordingly, electrochemical capacitors cannot replace batteries but can complement them in many applications. Applications that can benefit from electrochemical capacitors include medical, such as X-ray and MRI (magnetic-resonance imaging), spot and contact welding, audio-line stiffening, actuators, large electric motor starting and power quality such as initial pulse power for UPS systems.

Advantages:

1. Long life, can be cycled millions of time
2. Low cost per cycle and safe
3. Rapid charging – super capacitors charge in seconds
4. Extremely low internal resistance and extremely low heating rates

Disadvantages:

1. High self discharge - the rate is considerably higher than that of an electrochemical battery.
2. Cells have low voltages - serial connections are needed to obtain higher voltages.
3. Low energy density

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Applications of electrochemical capacitors

The major applications of electrochemical capacitors appear to be in high-pulse power and short-term power hold. Some applications of electrochemical capacitors are discussed below.

1. Memory back-up

Many appliances now incorporate digital components with memory where even a very brief interruption in the power supply could cause the loss of stored information. In such applications, the

capacitor can act as a back-up supply for short periods. Batteries are the alternative to the capacitors for these applications but batteries have a limited lifetime, and therefore need to be replaced regularly. Electrochemical capacitors are a preferred choice as back-up power supply due to their long lifetime.

2. Electric and hybrid electric vehicles

Battery-powered electric vehicles have the limitations of low power-density, limited charge/discharge cycles, high-temperature dependence, and long charging-time. Electrochemical capacitors are bereft of these limitations albeit they are faced with other limitations such as low energy-density and high costs. Peak-load requirements that result from accelerating or climbing up-hills could be met by the high-power device, namely the electrochemical capacitors bank. An electrochemical capacitor is presently the power supply in hybrid cars for start/stop application. When a hybrid vehicle stops, its internal combustion engine (ICE) shuts down which is restarted by the electrical system powered by an electrochemical capacitor that is recharged when the ICE resumes powering the vehicle. This helps reducing fuel consumption. Electrochemical capacitors are ideally suited for city-transit buses with stop-and-go driving, in trash trucks that can experience as many as a thousand start/stop cycles during a day, and in delivery vans that operate on similar drive cycles. The primary challenges for any energy storage unit used in heavy duty hybrid vehicles are the long cycle-life and the need to dissipate the heat generated due to charge/discharge losses. Electrochemical capacitors are highly efficient and have limited heat dissipation owing to their low-energy content.

3. Power quality:

Static-synchronous-compensator system injects or absorbs power from a distribution line to compensate for any voltage fluctuations. Such a system requires a DC energy storage device of some sort from which energy could be drawn or stored. Since the majority of voltage perturbations on the distribution bus are short-lived, usually not lasting more than 10 cycles, electrochemical capacitors are an attractive option for energy storage and delivery to improve the power quality.

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4. Battery improvement

Batteries are being used widely in the portable power appliances, such as UPS, laptops, and mobile phones. Many such devices draw high-power pulsed currents which result in the reduction of battery performance. Batteries in parallel with electrochemical capacitors could be an effective alternative for these applications.

5. Portable power supplies

Most devices presently using battery power supplies have long recharge time and need to be charged overnight. These need to be replaced with the electrochemical capacitors that can be quickly charged and discharged. Indeed, for any portable electronic equipment with moderate energy demands, electrochemical capacitors are ideally suited as rechargeable stand-alone power sources.

6. Renewable energy applications

In solar photovoltaic applications, batteries need to be replaced every 1–3 years because of continuous cycling that has a detrimental effect on batteries. But electrochemical capacitors can be charged and discharged quickly for large number of cycles, and need to be replaced every 20 years only, which is similar to the life-span of the photovoltaic panels. Life-cycle costs are therefore reduced by eliminating frequent maintenance requirements. Energy efficiency is always of primary concern in renewable power generation. In this regard electrochemical capacitors are attractive as they exhibit much higher charging efficiency than batteries.

7. Micro-scale energy scavenging systems

Products and systems can be designed around supercapacitor technology for efficient energy storage and its retrieval later. The concept is to generate electrical energy at anytime from see-saw, swing, health-club equipment, exercising equipment, etc., with little effort and its retrieval on demand.

Technology challenges

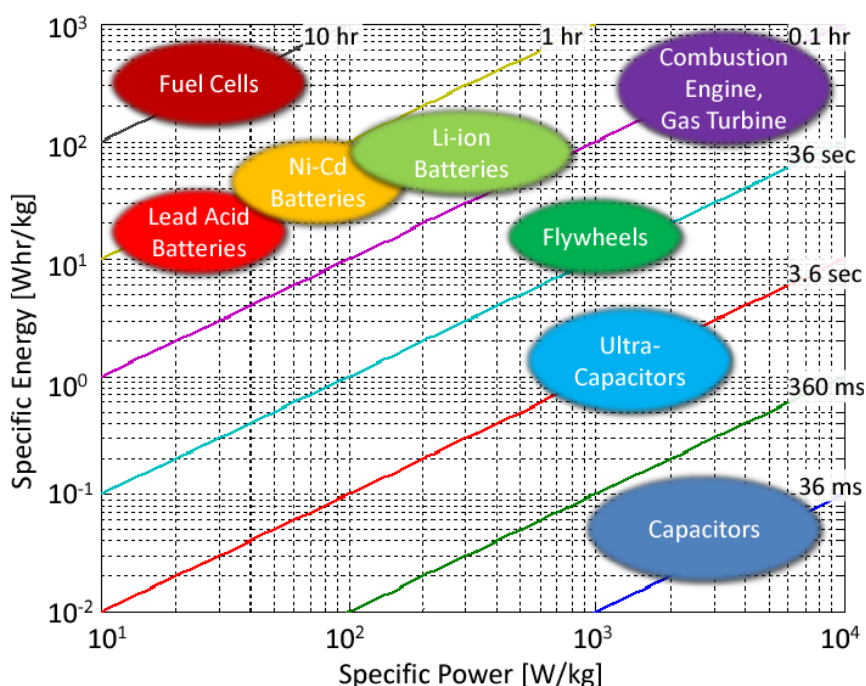
For many applications, relatively higher cost of electrochemical capacitors is currently the primary reason for not being the energy storage technology of choice. Despite their high-level of performance, electrochemical capacitors are simply too expensive to compete against the other available approaches. For some applications, potential users find electrochemical capacitors to be attractive but find their energy density to be too low. Hence increasing energy density and lowering cost are the primary challenges facing electrochemical capacitor developers.

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Ragone plot

A **Ragone plot** is a plot used for performance comparison of various energy-storing devices. On such a plot the values of energy density (in Whr/kg) are plotted versus power density (in W/kg). Both axes are logarithmic, which allows comparing performance of very different devices (for example, extremely high and extremely low power). Conceptually, the vertical axis describes how much energy is available, while the horizontal axis shows how quickly that energy can be delivered, otherwise known as power, per unit mass.

- Fuel cells have high energy density as the electroactive species can be continuously supplied but the power density is low due to slow kinetics of redox reactions at electrodes
- Battery systems offer moderate energy density and power density.
- Ultracapacitors (supercapacitors) can deliver very high power density as they can discharge a large amount of charge quickly (because no redox reaction is involved) but energy density is very limited because the charge cannot be stored for a long time



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