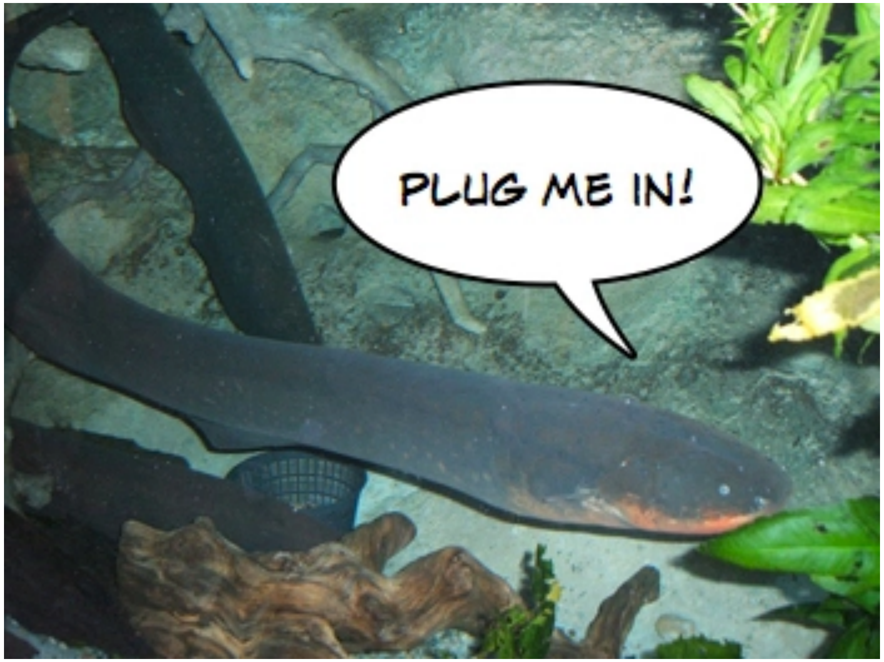
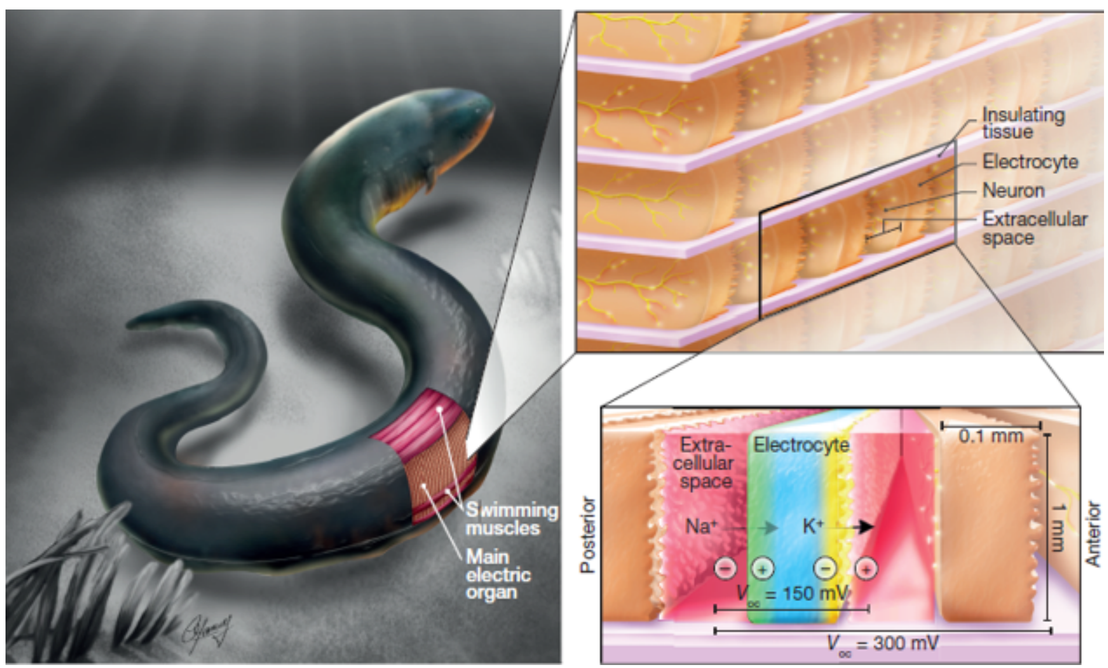
Electrochemistry

Electric Eel



Fundamentally, the eel is simply a living *battery*. As much as 80 per cent of its body is an electric organ, made up of many thousands of small platelets, which are alternately super-abundant in K^+ and Na^+. In effect, the voltage comprises thousands of concentration cells, each cell contributing a potential of about 160 mV.

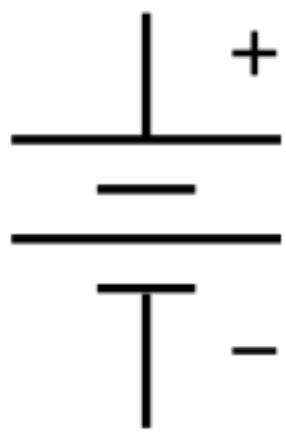
The eel causes the ionic charges on the surfaces of its voltage cells to redistribute and has the effect of summing the *emf* s of the mini-cells, in just the same way as we sum the voltages of small batteries incorporated within a *series circuit*. The ionic strength of seawater is very high, so conduction of the current from the eel to its prey is both swift and efficient.



Batteries and Fuel Cells

Module 4

- A Battery is a device that consists of one or more galvanic cells connected in series and/or parallel, which converts the chemical energy (redox reaction) to electrical energy in a stored form and can be used whenever required.



Terminology

1. EMF of a battery $\Delta G = -nFE$
2. Capacity: Total quantity of electricity that can be withdrawn from a full charged cell.
3. Energy Density: Voltage of the cell and amount of charge that can be stored.
4. Long Self life
5. Safety
6. Compact and light weight
7. Low price
8. Cycling

Types of batteries

- Primary battery (Primary cells)

  In which the cell reaction is not reversible. When all the reactants have been converted to product, no more electricity is produced and the battery is dead.

  Ex: Dry cell, Leclanché Cell

- Secondary battery (secondary cells)

  In which cell reactions can be reversed by passing electric current in the opposite direction. Thus it can be used for a large number of cycles.

  Ex: Lead-Acid Batteries, Ni-Cd, Li-ion

- Flow battery and fuel cell

  In which materials (reactants, products, electrolytes) pass through the battery continuously,

Primary Cell

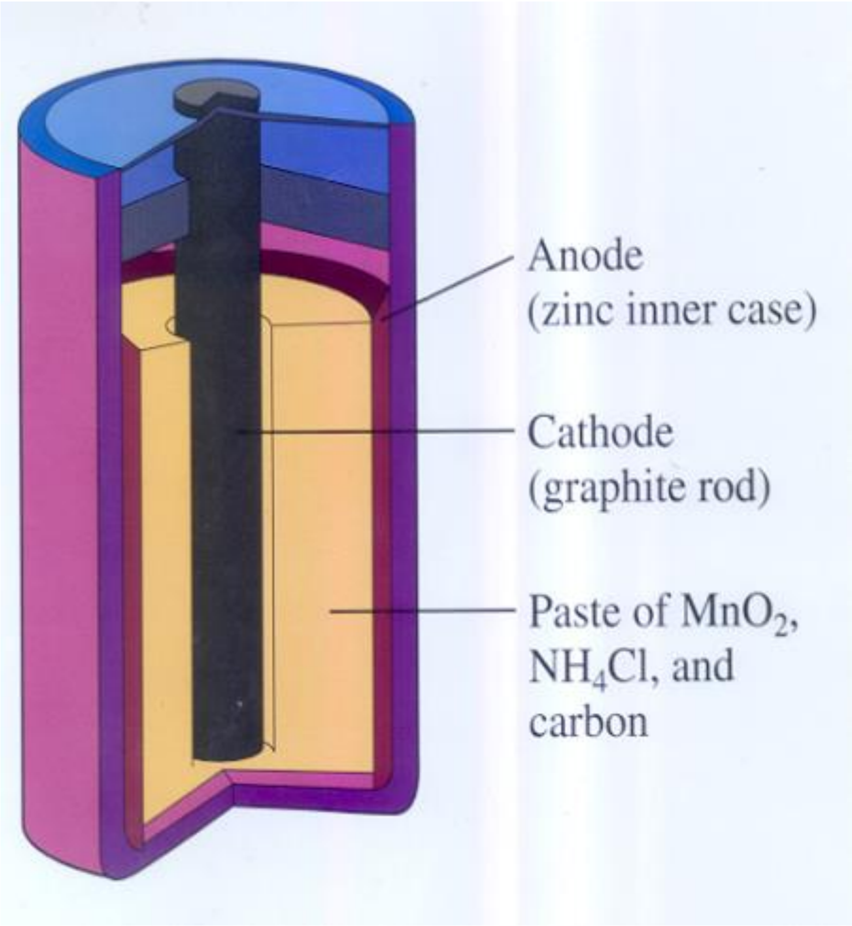
In our everyday experience, we know that some batteries are rechargeable, whereas others are used once and disposed of.

Single-use batteries that cannot be recharged are called primary cells or primary batteries.

Flashlights almost always rely on alkaline batteries, and many MP3 players or handheld video games can also use them.

One Hit Wonder!!!

Leclanché Cell



The venerable carbon-zinc cell or Leclanché cell was invented in 1866 by Georges Leclanché and was the most common small battery throughout most of the 20th century

Representation: $Zn \mid Zn^{2+} \mid\mid NH_4^{+} \mid MnO_2 \mid C$

Anodic reaction : $Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathodic reaction: $2\,MnO_2(s) + 2\,H_2O(l) + 2e^- \rightarrow 2\,MnO(OH)(s) + 2\,OH^-$

Net Cell Reaction : $Zn(s) + 2MnO_2\,(s) + 2H_2O(l) \rightarrow 2MnO(OH)(s) + Zn^{2+} + 2OH^-$

Drawbacks:

- Some of the complexity of this reaction comes from the fact that the reduction of the ammonium ion produces two gaseous products

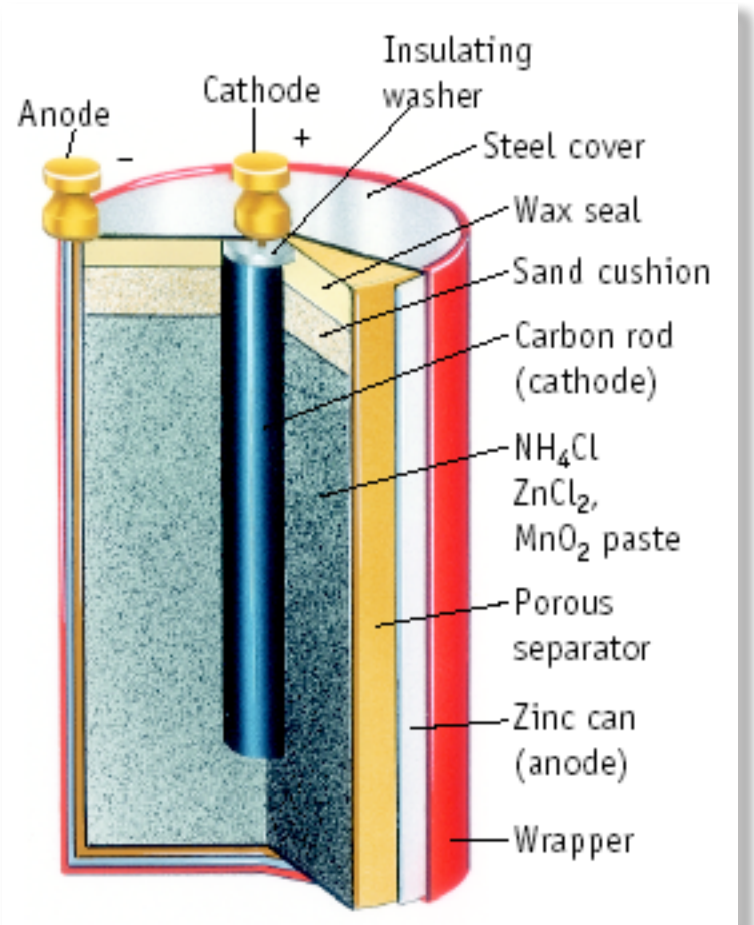
$$2NH_4^+{}_{(aq)} + 2e^- \rightarrow 2NH_{3(g)} + H_{2\ (g)}$$

which must be absorbed to prevent the buildup of gas pressure.

MnO_2 in the cell removes the H_2 according to the following reaction:

$$2MnO2(s) + H2(g) \rightarrow Mn2O3(s) + H2O(l)$$

Zn-Carbon Dry Cell



- A dry cell has the electrolyte immobilized as a paste, with only enough moisture in it to allow current to flow.
- Unlike a wet cell, a dry cell can operate in any orientation without spilling, as it contains no free liquid.
- The potential is 1.50 V.
- The carbon powder will increase the electrical conductivity of the MnO_2 and retain the moisture of the electrolyte.

Cathode: $2\ NH_4(aq) + 2\ MnO_2(s) + 2\ e^- \rightarrow\ Mn_2O_3(s) + 2\ NH_3(g) + H_2O(l)$

Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Applications and Disadvantages

- Used in flash lights, transistor radios, calculators etc

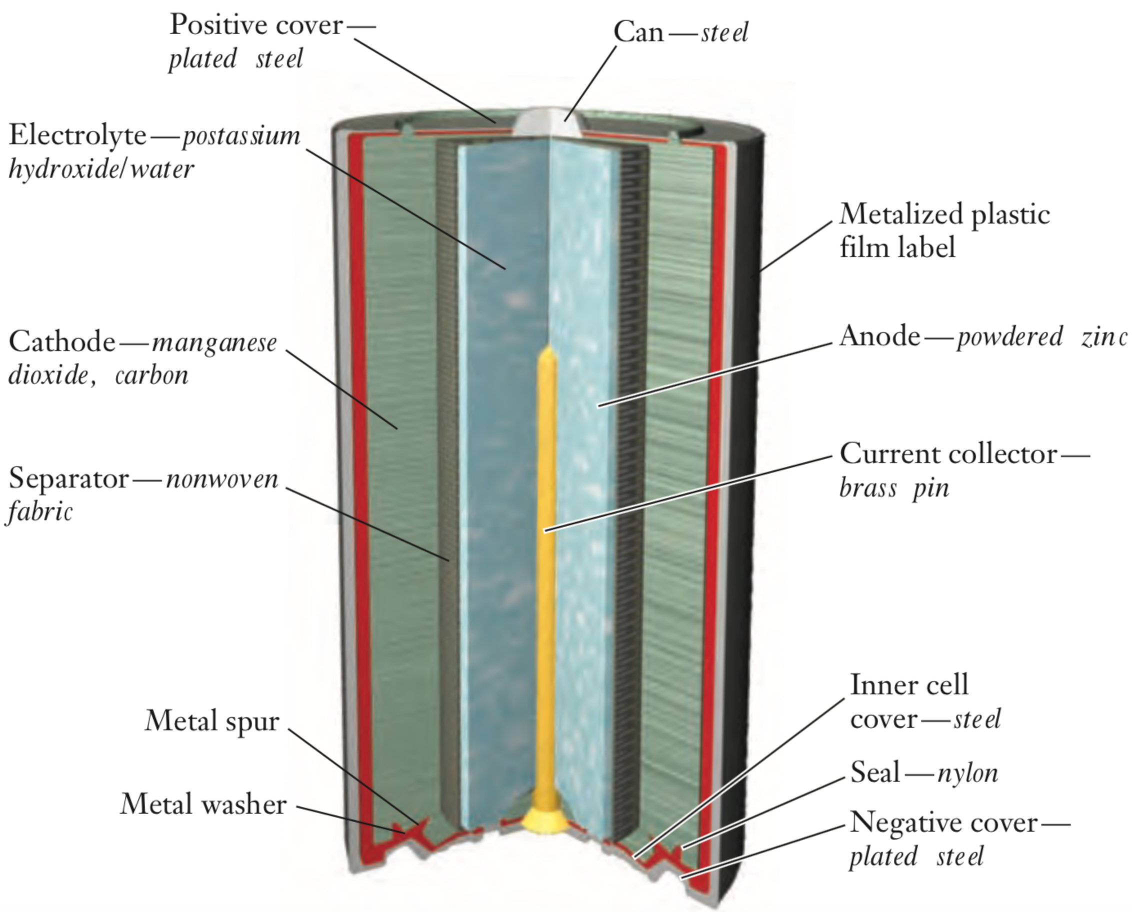
<u>Disadvantages of dry cell</u>

- The voltage of this cell is initially about 1.5 volts, but decreases as energy is taken from the cell. Due to the accumulation of the products on electrodes. It also has a short shelf life and deteriorates rapidly

- Oxidation of the zinc wall eventually causes the contents to leak out, so such batteries should not be left in electric equipment for long periods

Alkaline Battery

The most prevalent type of primary battery in use today is the alkaline battery.



Alkaline Battery

- The anode in an alkaline battery is a zinc electrode, and the oxidation half- reaction can be written:

$$Zn(s) + 2\ OH^{-}(aq) \rightarrow ZnO + H_2O(l) + 2\ e^{-}$$

- The cathode is derived from manganese(IV) oxide, and the half-reaction is

$$2\ MnO_2(s) + H_2O(l) + 2\ e^{-} \rightarrow Mn_2O_3(s) + 2\ OH^{-}(aq)$$

- We can combine these two half-reactions to yield a net equation that represents the chemistry of an alkaline dry cell battery.

$$Zn(s) + 2\ MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$$

Alkaline Battery

The essential design features of an alkaline battery:

- The electrolyte used is KOH, but rather than dissolving the electrolyte in liquid water, it is in the form of a paste or a gel—hence the term dry cell.

- The MnO_2 for the cathode is mixed with graphite to increase conductivity.

- The anode is a paste containing powdered zinc. (Powdering the zinc increases the surface area and improves performance.)

- The battery case is also important in the design. Electrons generated by oxidation are collected by a piece of tin-coated brass connected to the bottom of the battery case. The remainder of the battery case is in contact with the cathode, but a protrusion on top makes it easier for a consumer to identify the positive terminal.

Alkaline Battery

Alkaline batteries are prone to leaking potassium hydroxide, a caustic agent that can cause respiratory, eye and skin irritation.

<u>This can be avoided by</u>

- Not attempting to recharge disposable alkaline cells,
- Not mixing different battery types in the same device,
- Replacing all of the batteries at the same time,
- storing in a dry place.

<u>Caution</u>

- Once a leak has formed due to corrosion of the outer steel shell, potassium hydroxide forms a feathery crystalline structure that grows and spreads out from the battery over time, following up metal electrodes to circuit boards where it commences oxidation of copper tracks and other components, leading to permanent circuitry damage.

- The leaking crystalline growths can also emerge from seams around battery covers to form a furry coating outside the device, that corrodes any objects in contact with the leaking device.

Mercury Battery

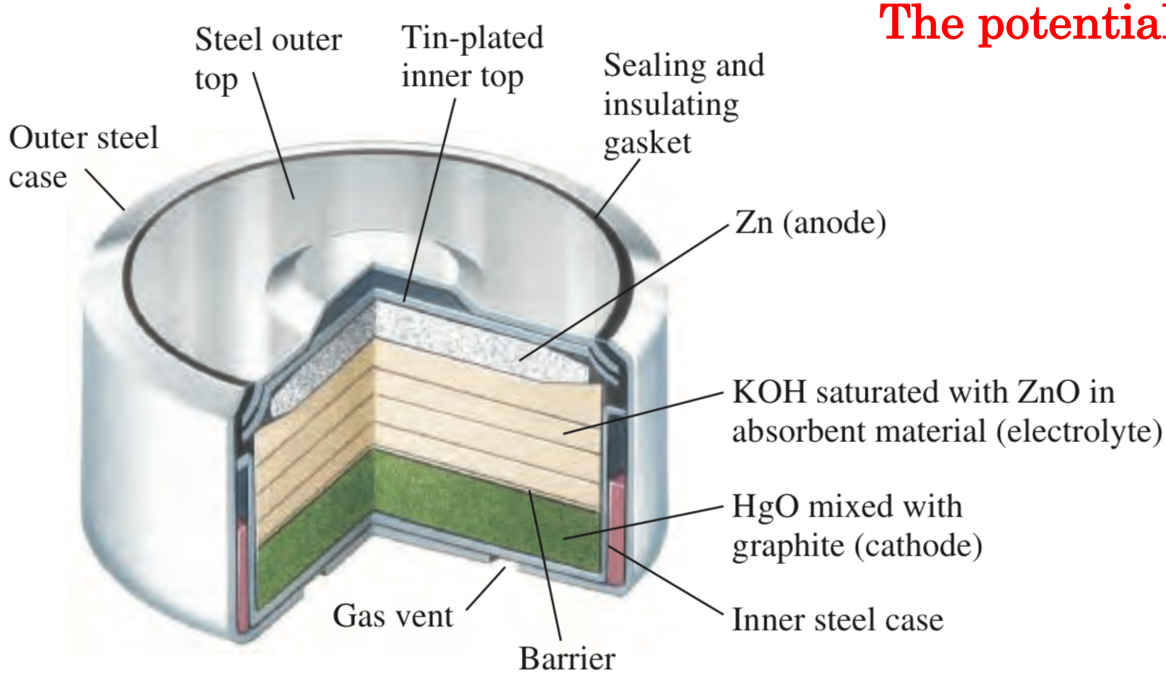
- For a medical device, such as a heart pacemaker, a battery should not only be small but long lasting. Mercury batteries have come to fill this role.

- The mercury battery (also called a zinc-mercuric oxide cell) shown here has a voltage output that is extremely stable over long times.

Anode: $Zn(s) + 2\ OH^-(aq) \rightarrow Zn(OH)_2(s) + 2\ e^-$

Cathode: $HgO(s) + H_2O(l) + 2\ e^- \rightarrow Hg\ (l) + 2\ OH^-(aq)$

The potential is 1.35 V



Mercury Battery

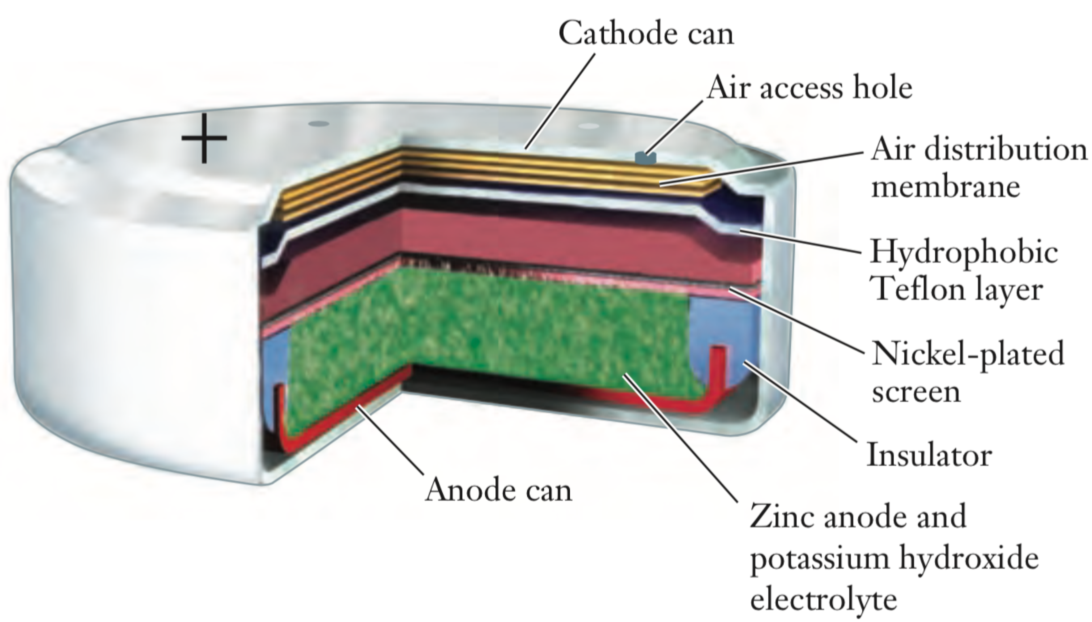
- These batteries are commonly used in devices where frequent battery changes would be a nuisance or hazard.
- In a mercury battery, sodium hydroxide or potassium hydroxide is used as an electrolyte.
- Sodium hydroxide cells have nearly constant voltage at low discharge currents, making them ideal for hearing aids, calculators, and electronic watches.
- Potassium hydroxide cells, in turn, provide constant voltage at higher currents, making them suitable for applications requiring current surges, such as photographic cameras with flash and watches with a backlight.

Zinc-air Battery

- These batteries are sold as single-use, long lasting products for emergency use in cellular phones.

- In a zinc-air battery, one of the reactants is oxygen from the surrounding air. They can also be kept on hand in sealed bags and charged when needed by opening the bag to expose the battery to air.

Anode: $Zn(s) + 2\ OH^{-}(aq) \rightarrow Zn(OH)_2(s) + 2\ e$
Cathode: $\frac{1}{2}\ O_2\ (g) + H_2O(l) + 2\ e^{-} \rightarrow 2\ OH^{-}$



- There are obstacles to the widespread use of this technology because environmental factors, such as humidity, affect its performance.

Primary Lithium batteries

- One of the main attractions of lithium as an anode material in its position as the most electropositive metal in the electrochemical series combined with its low density, thus offering the largest amount of electrical energy per unit weight among all solid elements.

- Li cannot be used with the traditional aqueous electrolytes due to the very vigorous corrosive reaction between Li and water with inflammable hydrogen as the product.

- In the 1980s progress was made in the use of Li as an anode material with MnO_2, liquid SO_2 (or) thionyl chlorides as the cathode, and hexafluorophosphate dissolved in propylene carbonate as a typical organic electrolyte.

Li Primary batteries

Li Cells with solid cathode | Li Cells with Soluble cathode | Li Cells with Solid electrolyte

Li Cells with solid cathode

3 to 3.2 V

High energy density, good low-temperature performance; cost effective. Small in size, long self life,

Electrical medical devices; memory circuits

Anode: Li,

Cathode: MnO_2 or V_2O_5 mixed with 10% graphite

Electrolyte: Lithium salt in organic solvent

Cathode: $Mn^{4+} \rightarrow Mn^{3+}$

$V^{5+} \rightarrow V^{4+}$

Li Cells with Soluble cathode:

Anode: Li,
Cathode: $SO_{2;}$ $SOCl_2$or SO_2Cl_2 dissolved in electrolyte
Electrolyte: Lithium salt in organic solvent

Cathode: $2SO_2 + 2e^- \rightarrow S_2O_4^{2-}$

$$2SOCl_2 + 4e^- \rightarrow 4Cl^- + S + SO_2$$

$$SO_2Cl_2 + 2e^- \rightarrow 2Cl^- + SO_2$$

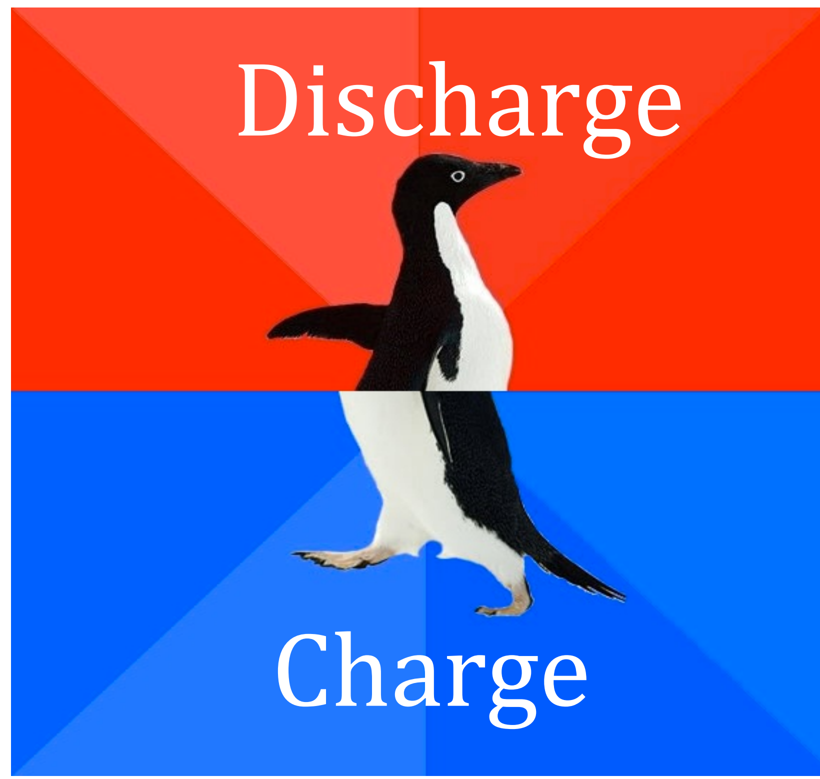
Li Cells with Solid Electrolyte:

Anode: Li,
Cathode: TiS2, V2O5
Electrolyte: Solid electrolyte Such as LiX in PEO (Polyethylene oxide)

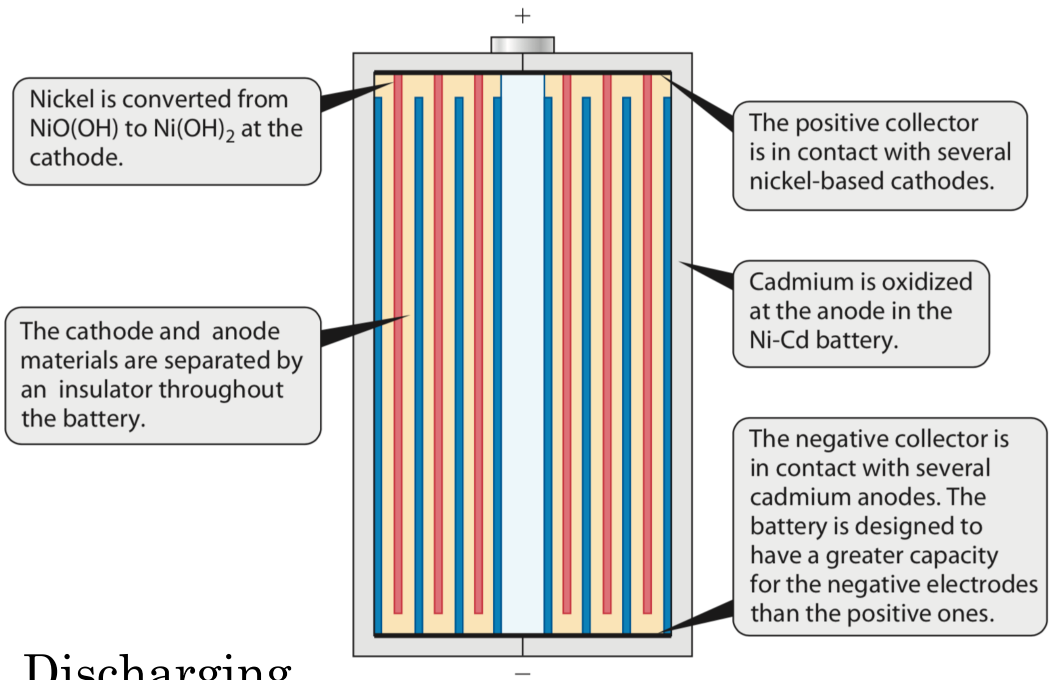
Long Life due to no evaporation of electrolyte

Secondary Cell

- Rechargeable batteries are examples of secondary cells or secondary batteries.



Ni – Cd Battery



Electrolyte: KOH

Discharging

<u>At anode:</u> $Cd_{(s)} + 2\,OH^- \rightarrow Cd(OH)_{2(s)} + 2e^-$

<u>At cathode :</u> $2NiO(OH) + 2H_2O_{(l)} + 2e^- \rightarrow 2\,Ni(OH)_{2\,(s)} + 2\,OH^-_{(aq)}$

<u>Net reaction:</u> $2\,NiO(OH)_{(s)} + Cd_{(s)} + 2\,H_2O_{(l)} \Leftrightarrow Cd(OH)_{2(s)} + 2\,Ni(OH)_{2(s)}$

Discharge and Charge Chemistry

- Ni-Cd batteries can be expended and recharged many times, but they are sometimes susceptible to a performance-decreasing **memory effect**, inability to use all of the possible chemical energy of the battery unless it is completely discharged. So successive recharging ultimately results in shorter times before the battery appears to die.

- Memory effect is caused due to the formation of a thin layer of material on the electrodes inside the battery, limiting the redox reactions in the cell.

Advantages

- Constant voltage (1.4V)

- No gaseous products

- Wide temperature range (Up to 70°C)

- Charging process is strongly endothermic. The battery cools during charging. This makes it possible to charge very quickly.

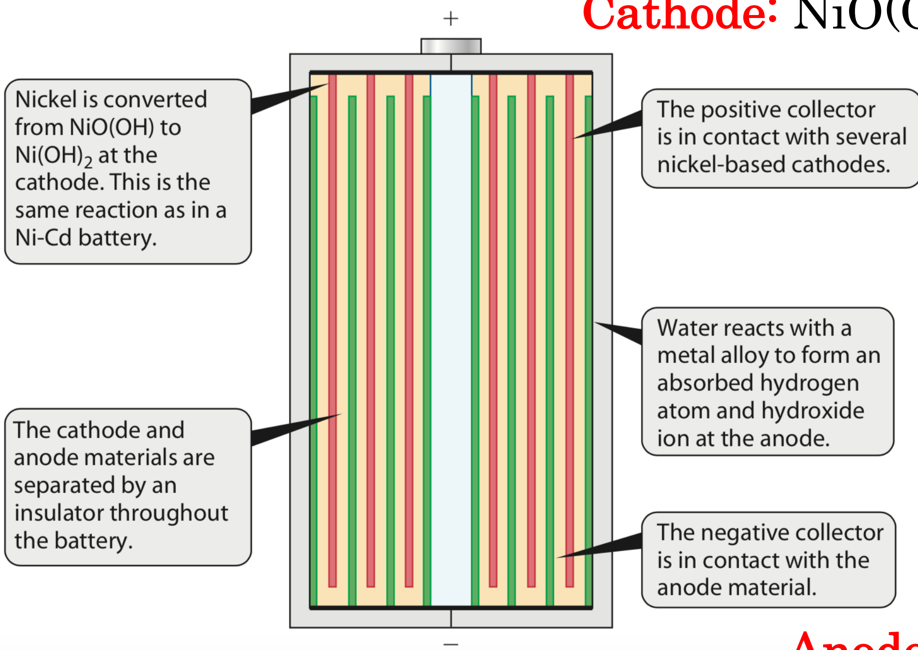
Applications

- Motorized equipment
- Power tools
- Transistors
- Electronic calculators
- Commercial and industrial portable products
- Medical instrumentation
- Emergency lighting
- Toys
- Cordless and wireless telephones

- Medical equipment
- Personal care
- Professional lighting
- Radio communication
- Professional tooling
- Military equipment
- Professional electronic devices

Ni – Metal-hydride Battery

Cathode: $NiO(OH)_{(s)} + H_2O_{(l)} + e^- \rightarrow Ni(OH)_{2(s)} + OH^-$



Electrolyte: KOH

Cell voltage is 1.2-1.5 V

Anode: $MH_{(s)} + 2\ OH^-_{(aq)} \rightarrow M_{(s)} + H_2O_{(l)} + 2\ e^-$

- Nickel-metal-hydride batteries find use in many of the same devices as Ni-cad cells, and larger versions serve as the main batteries in hybrid cars.

- Anode is made metal hydride, usually alloys of Lanthanum and rare earths that serve as a solid source of reduced hydrogen that can be oxidized to form protons. Some of the alloys used in commercially available Ni-metal-hydride batteries contain as many as seven different metals.

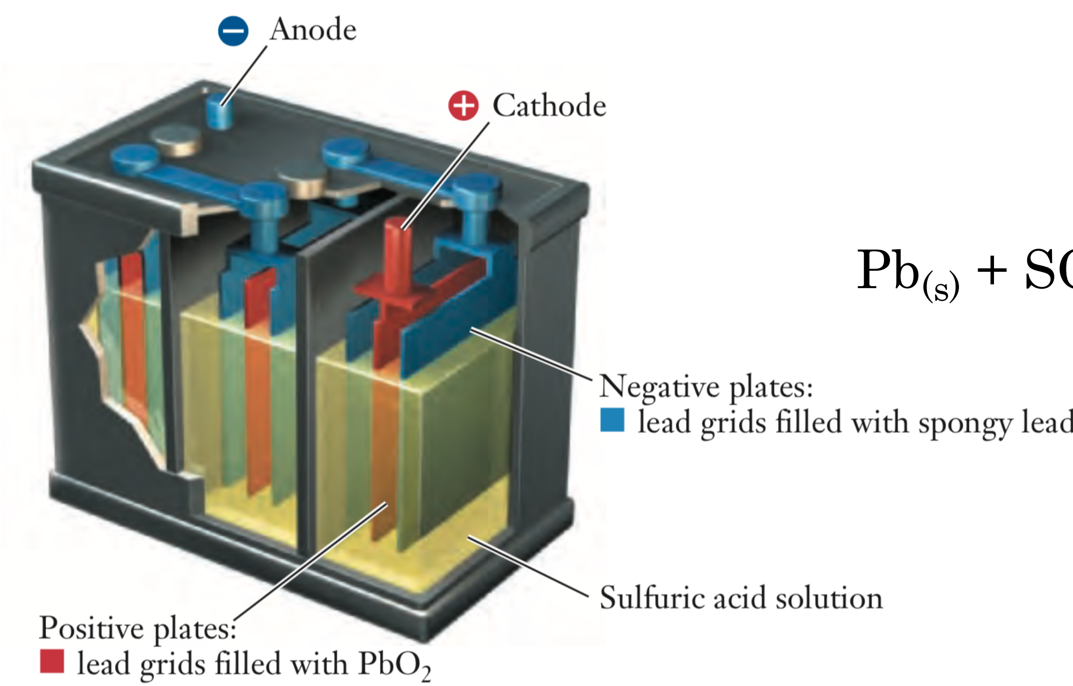
Lead-acid Storage Battery

- The most widely selling rechargeable batteries are the lead storage batteries in automobiles, which have been using the same technology for roughly 100 years.

Lead-acid Storage Battery

- The electrolyte for this battery is sulfuric acid.

- Sulfate ion is converted to $HSO4^-$ under the highly acidic conditions of the battery. Because of the importance of sulfuric acid in these batteries, they are sometimes referred to as **lead-acid storage** batteries.



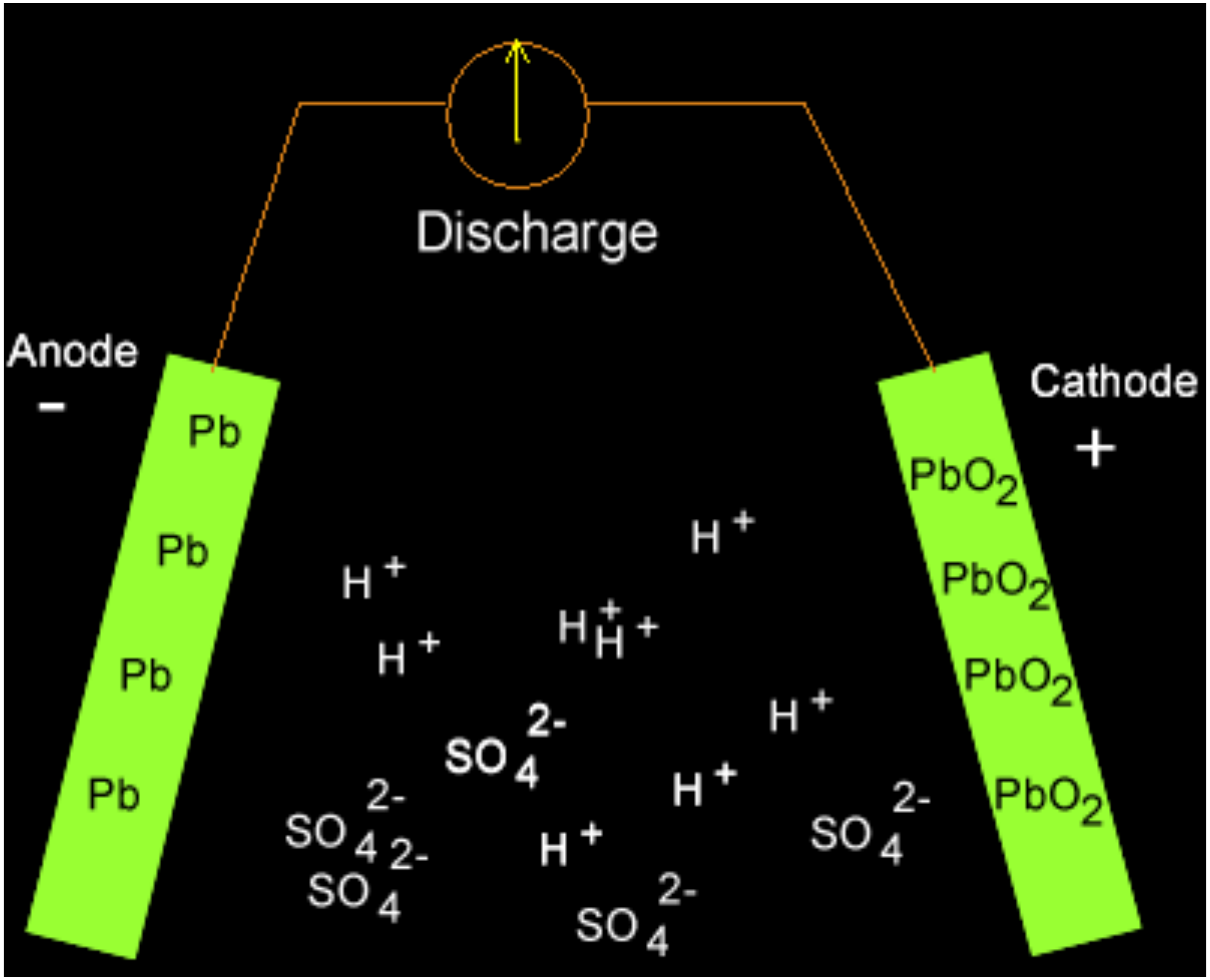
Anode:

$$Pb_{(s)} + SO_4{}^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2\ e^-$$

$$E_{cell} = 2.0\ V$$

Cathode: $PbO_{2(s)} + 4\ H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 2\ e^- \rightarrow PbSO_{4(s)} + 2\ H_2O$

Representation of Lead Storage Cell : **$Pb, PbSO_{4(s)} \mid H_2SO_{4\ (aq)} \mid PbO_{2(s)}, Pb$**


Discharge
Anode
−
Cathode
+
Pb
Pb
Pb
Pb
PbO2
PbO2
PbO2
PbO2
H +
H +
H +
H +
H +
H +
H +
H +
SO 4 2-
SO 4 2-
SO 4 2-
SO 4 2-
SO 4 2-

Lead-acid Storage Battery

- $E_{cell} = 2$ V.
- For a standard 12-V automobile battery, connect six cells wired in series.
- These batteries are rechargeable because the $PbSO_4$ produced adhere to the electrode surfaces. Passing electric current (obtained from the alternator of the automobile) to drive the redox reactions in the nonspontaneous direction recharges the battery.
- Driving the reactions in a battery in the reverse direction to recharge it sometimes requires a larger voltage than the discharge voltage to ensure that all chemical species are returned to their original states.
- Eventually, as the battery experiences mechanical shocks from bumping and jarring during the normal use of a car, $PbSO_4$ falls away from the electrodes. Eventually the battery can no longer be recharged and must be replaced.

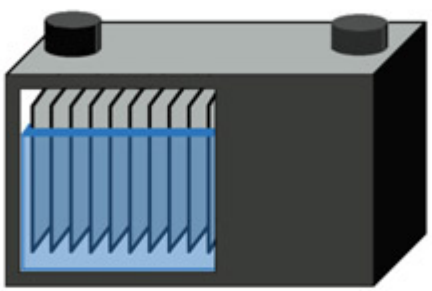
Sulfation

- Sulfation happens inside Lead–acid batteries when the electrolyte starts to break down. As the sulphuric acid splits up, sulfur ions become free forming crystals. These sulfur ion crystals then stick to the lead plates of the battery, thus forming lead sulfate crystals. With time the crystals grow in size and become hard, covering the lead plates completely. This coverage deteriorates the overall efficiency and power storage capability of the battery.

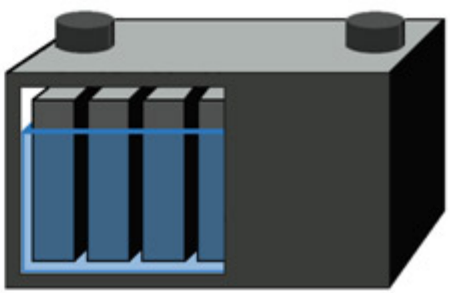
•Battery lying idle for several days between charges
•Battery is stored without any type of energy input
•Low electrolyte levels which expose plates to air
•Undercharging battery
•Incorrect charging levels

Lead-acid Storage Battery

- Pure lead is too soft and would not support itself, so small quantities of other metals are added to get the mechanical strength and improve electrical properties. The most common additives are antimony, calcium, tin and selenium. These batteries are often known as “lead-antimony” and “leadcalcium.”

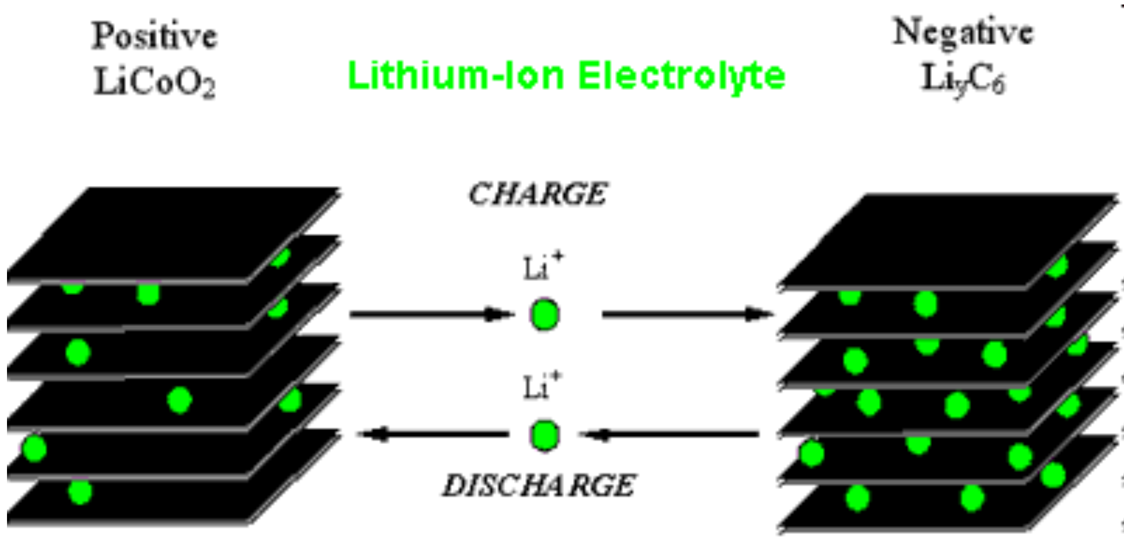


Starter battery



Deep-cycle battery

Secondary Lithium Ion Batteries



Composition

Anode

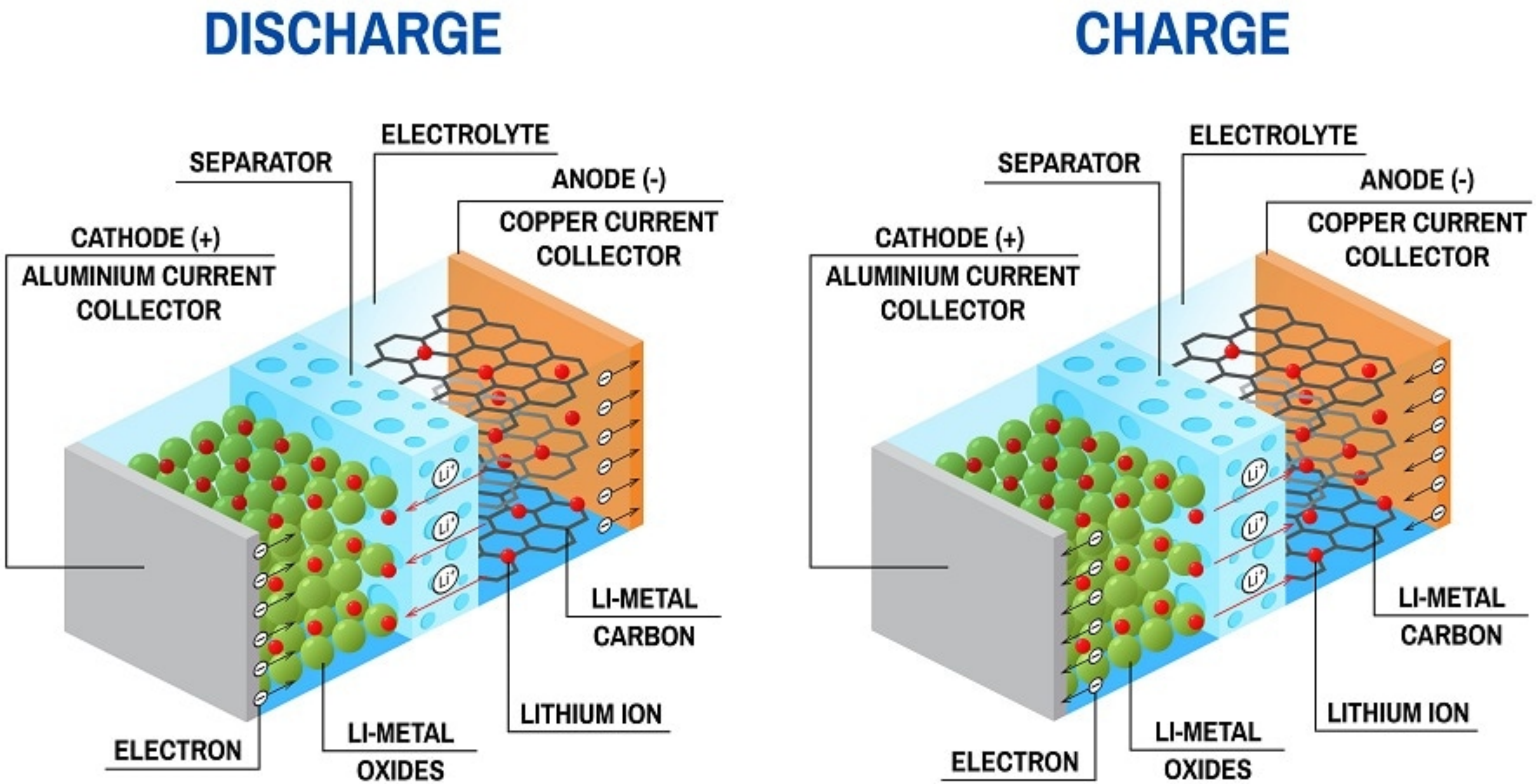
- Carbon based.
- This lithium content is lower then would be ideal, however higher capacity carbons pose safety issues.

Electrolyte

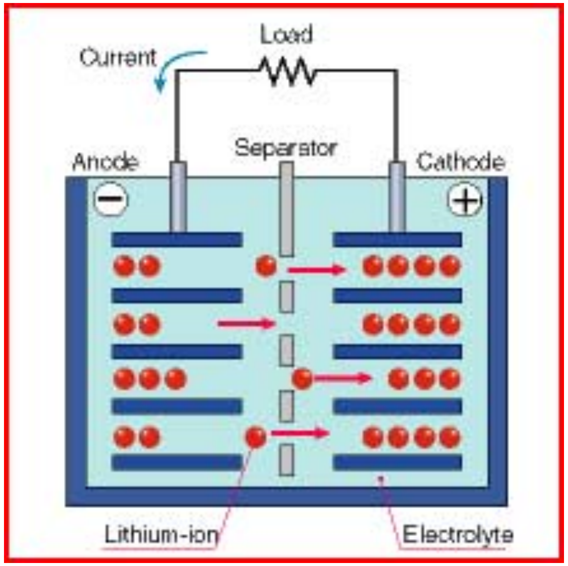
- Since lithium reacts violently with water, and the cell voltage is so high that water would decompose, a non-aqueous electrolyte must be used.
- A typical electrolyte is $LiPF_6$ dissolved in an ethylene carbonate and dimethyl carbonate mixture.
- Polymer electrolyte

Cathode materials

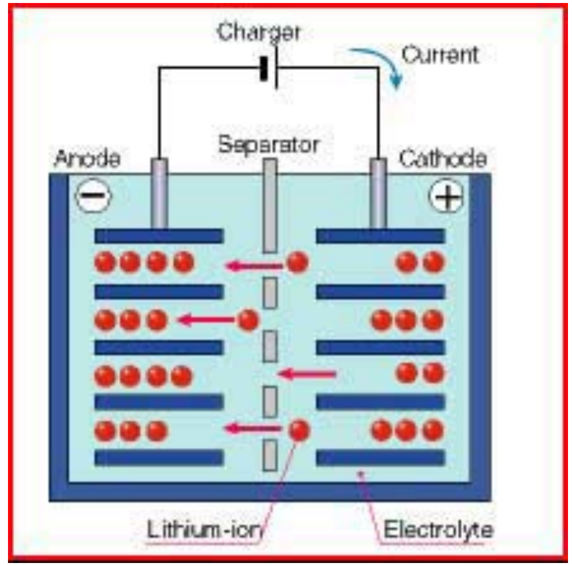
- The most common compounds are $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$.
- Of these, $LiCoO_2$ has the best performance but is very high in cost, is toxic and has a limited lithium content
- $LiNiO_2$ is more stable, however the nickel ions can disorder.
- $LiMn_2O_4$ is generally the best value for money, and is also better for the environment.


DISCHARGE
CHARGE
ELECTROLYTE
SEPARATOR
ANODE (-)
COPPER CURRENT COLLECTOR
CATHODE (+)
ALUMINIUM CURRENT COLLECTOR
LI-METAL CARBON
LITHIUM ION
ELECTRON
LI-METAL OXIDES
Li+
ELECTROLYTE
SEPARATOR
ANODE (-)
COPPER CURRENT COLLECTOR
CATHODE (+)
ALUMINIUM CURRENT COLLECTOR
LI-METAL CARBON
LITHIUM ION
ELECTRON
LI-METAL OXIDES
Li+

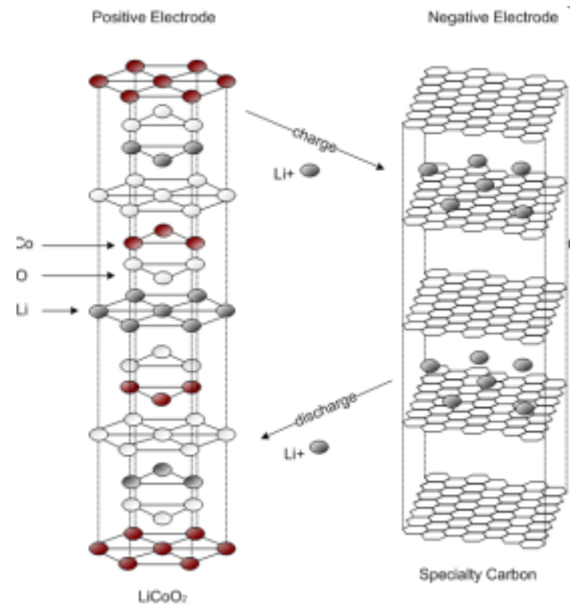
Working



Charging



Discharging



The following reactions take place upon working

Cathode: $$LiCoO_2 \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} Li_{1\text{-}x}CoO_2 + xLi^+ + xe^-$$

Anode: $$xLi^+ + C + Xe^- \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} CLi_x$$

Overall: $$LiCoO_2 + C \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} Li_{1\text{-}x}CoO_2 + Li_xC$$

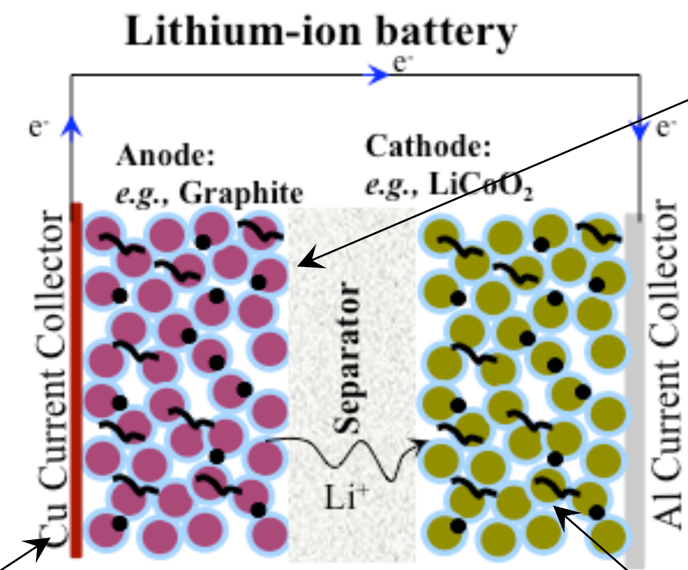
Chemistry and Construction

- Anode here is a non-metallic compound, e.g. carbon, which can store and exchange lithium ions.
- A lithium ion-accepting material (Intercalation), for example CoO_2, is then used as the cathode material, and lithium ions are exchanged back (deintercalation) and forth between the two during discharging and charging. These are called intercalation electrodes.
- This type of battery is known as a "rocking chair battery" as the ions simply "rock" back and forth between the two electrodes.

Discharge Process of a Conventional Lithium-Ion Battery Cell

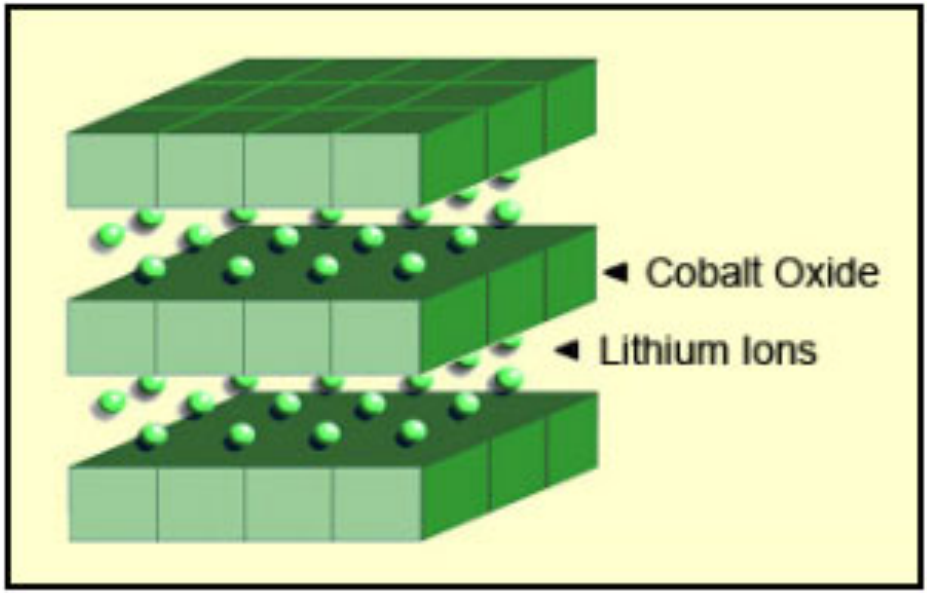
Lithium ion-battery

Electrolyte:
- Liquid organic solvents
- Polymers
- Gels

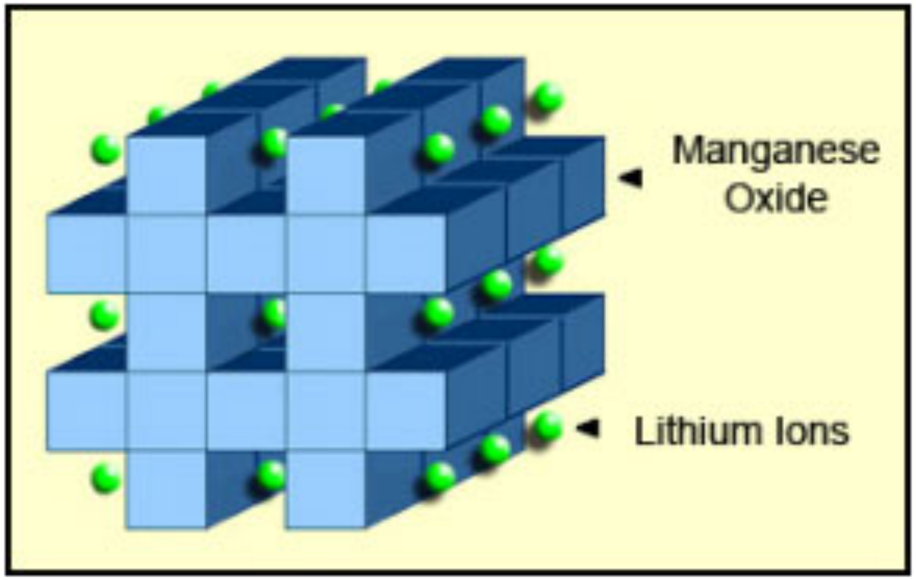


Anode:
- Carbon-based
- Alloys and intermetallics
- Oxides
- Lithium-metal

Cathode:
- Transition-metal oxides

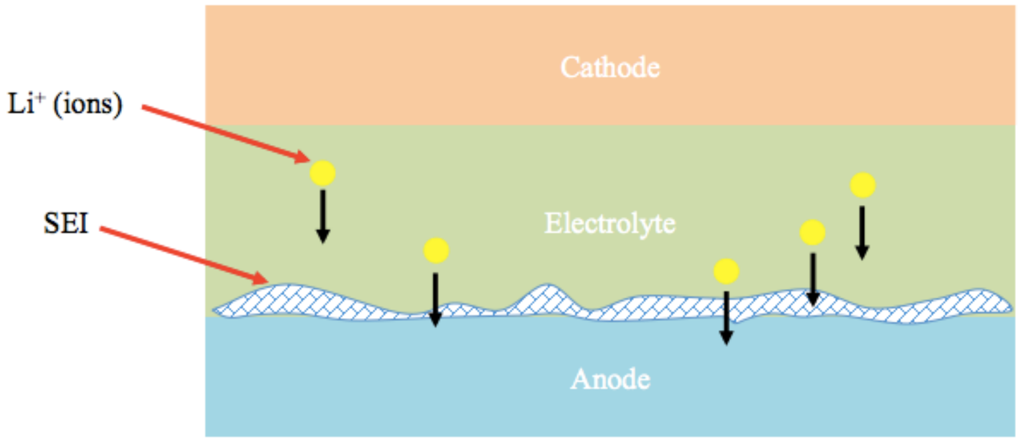


Li-cobalt structure.

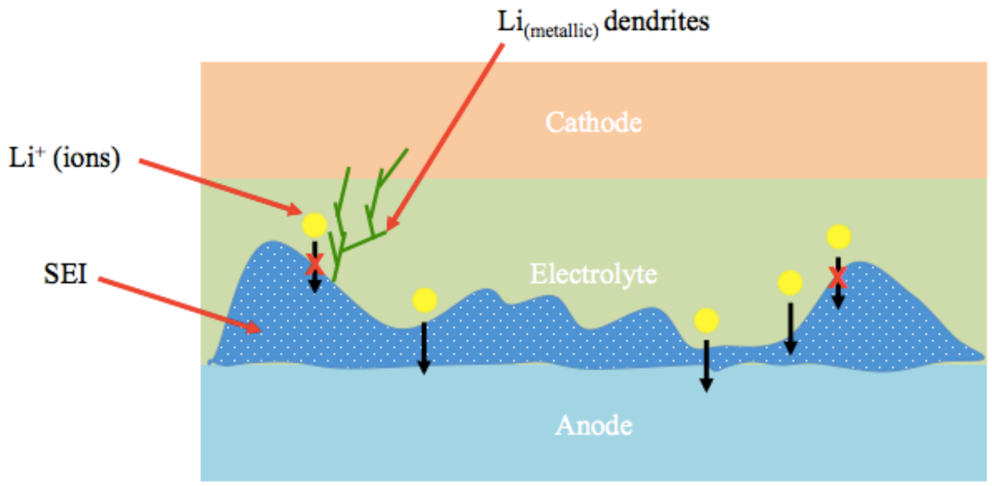


Li-manganese structure

Lithium Dendrite Formation

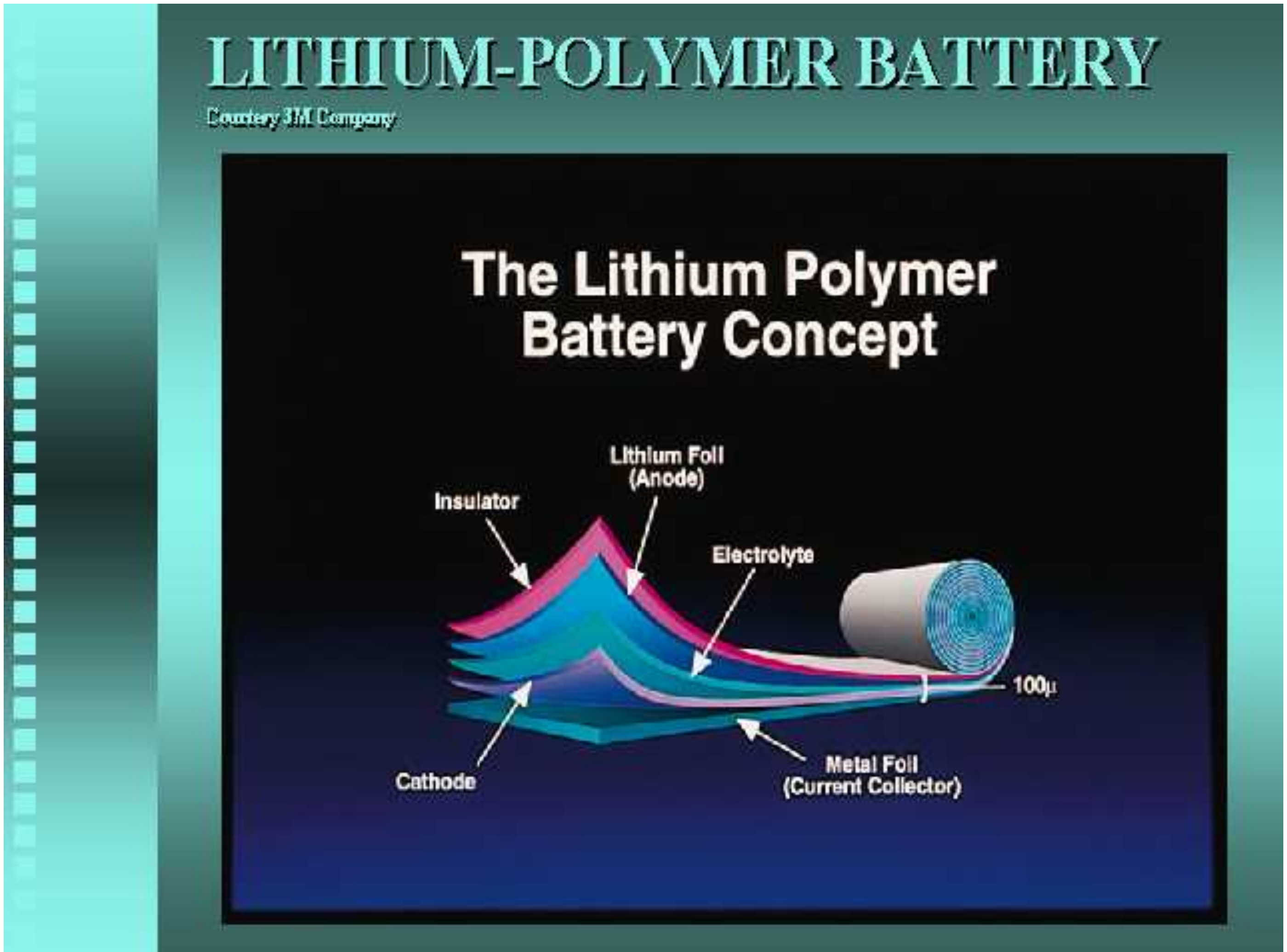


$$Li^+ + e^- \rightarrow Li_{(metallic)}$$

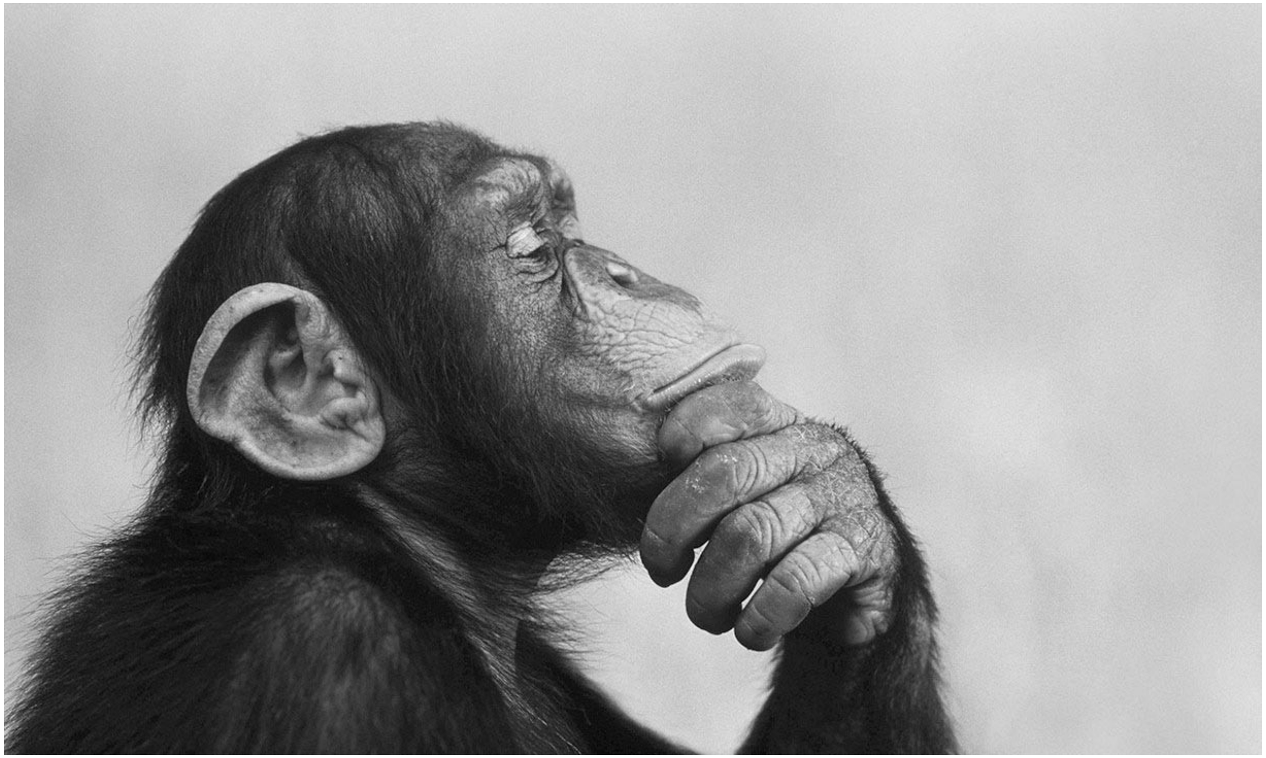


Lithium Polymer Battery

Electrolyte is a polymer



Fuel Cells



Fuel Cells

An electrochemical cell in which the energy of a reaction between a fuel (such as liquid hydrogen) and an oxidant (such as liquid oxygen) is converted directly and continuously into electrical energy.

Fuel cell: Operates with continuous replenishment of fuels at electrodes which doesn't require charging.

Representation: Fuel | electrode | electrolyte | electrode | Oxidant

At Anode: Fuel $\rightarrow$ Oxidized product + ne^-
At Cathode: Oxidant + ne^- $\rightarrow$ reduced product

Fuel Cells

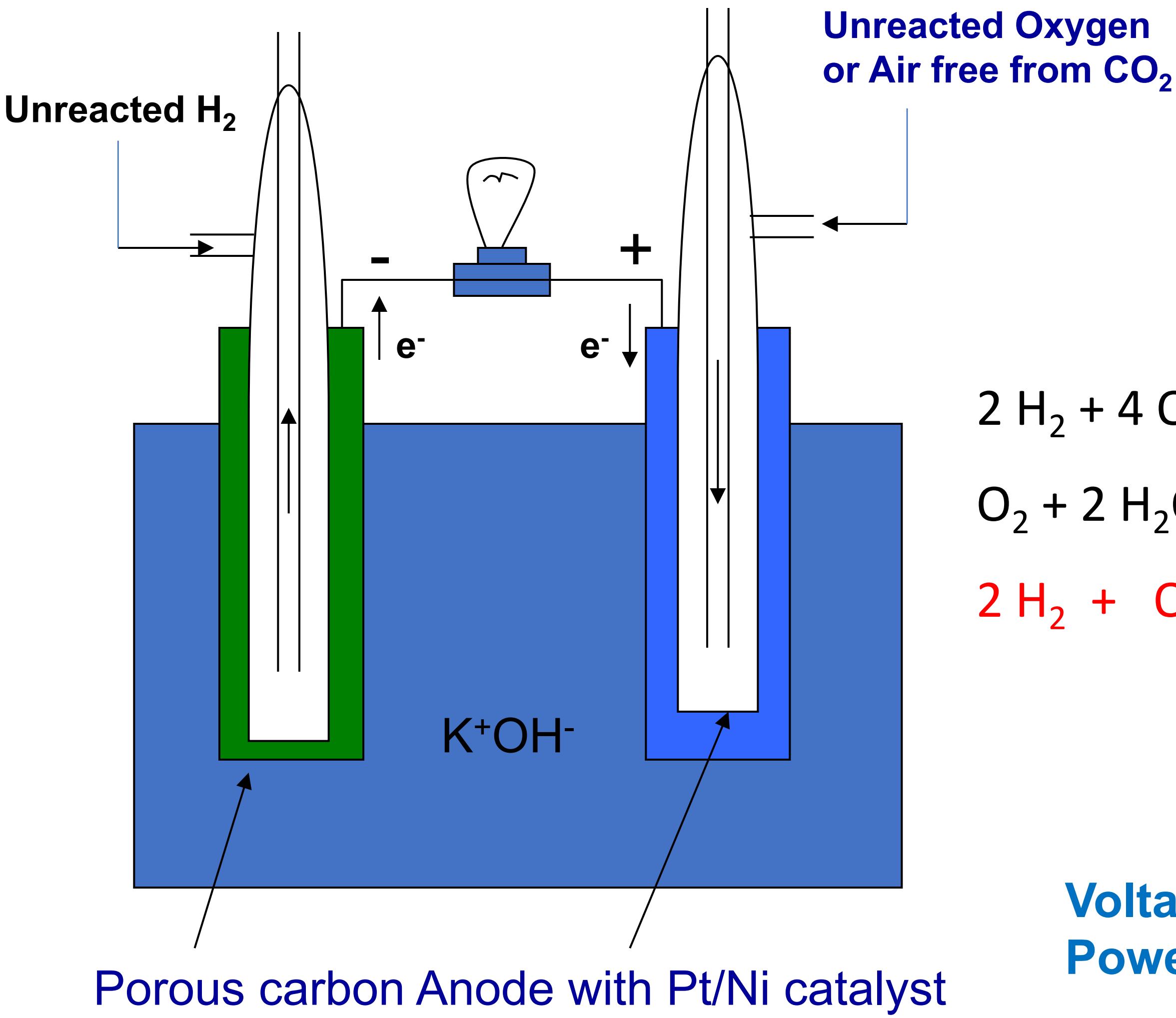
Classification :

1. Low Temperature fuel cells (< $100^{o}C$)
2. Moderate Temperature fuel cells (100 to $250^{o}C$)
3. High Temperature fuel cell (> $500^{o}C$)

Types :

- Alkaline Fuel Cells (AFC): US spacecraft
- Phosphoric Acid Fuel Cells (PAFC): Stationary power generation, city buses
- Molten Carbonate Fuel Cells (MCFC): Military application, power plants
- Polymer Electrolyte Membrane Fuel Cells (PEMFC): Car, Bus
- Solid Oxide Fuel Cells (SOFC): Industry
- Biochemical Fuel cells (BCFC)

Alkaline Fuel Cells (or) H_2- O_2 Fuel Cells

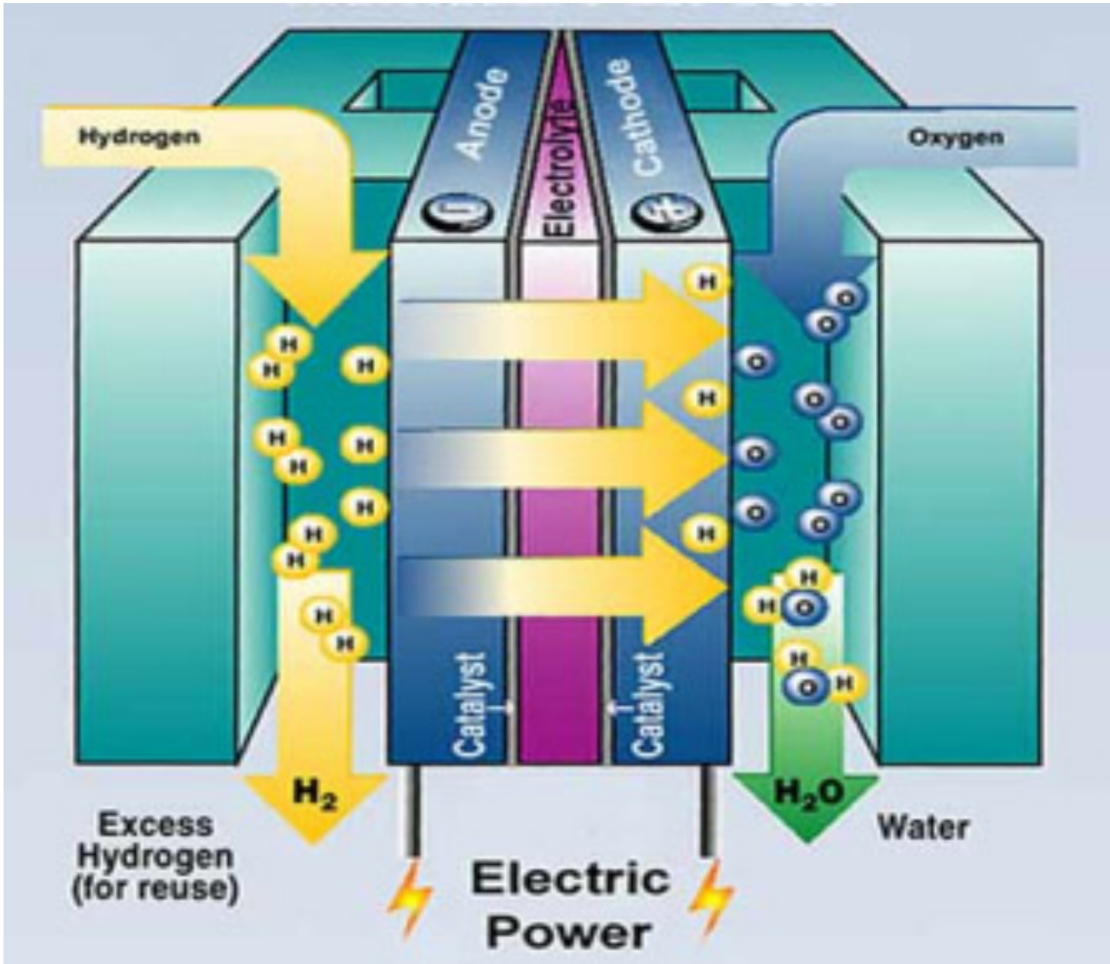


$2\,H_2 + 4\,OH^- \rightarrow H_2O + 4\,e^-$ (Anode)

$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$ (Cathode)

$2\,H_2 + O_2 \rightarrow 2\,H_2O$ (Net reaction)

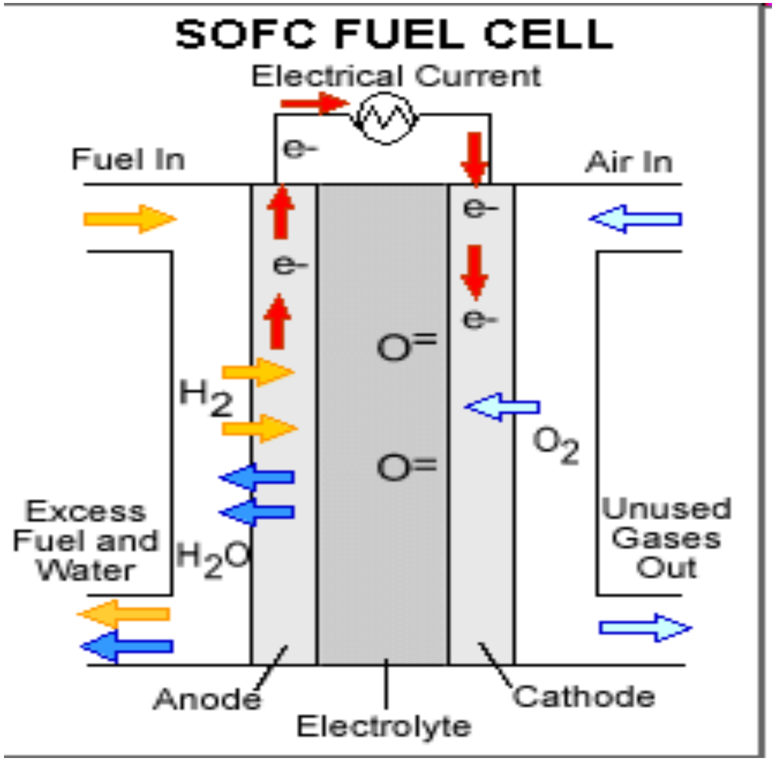
Voltage: 1.15 V
Power: 10-100 KW

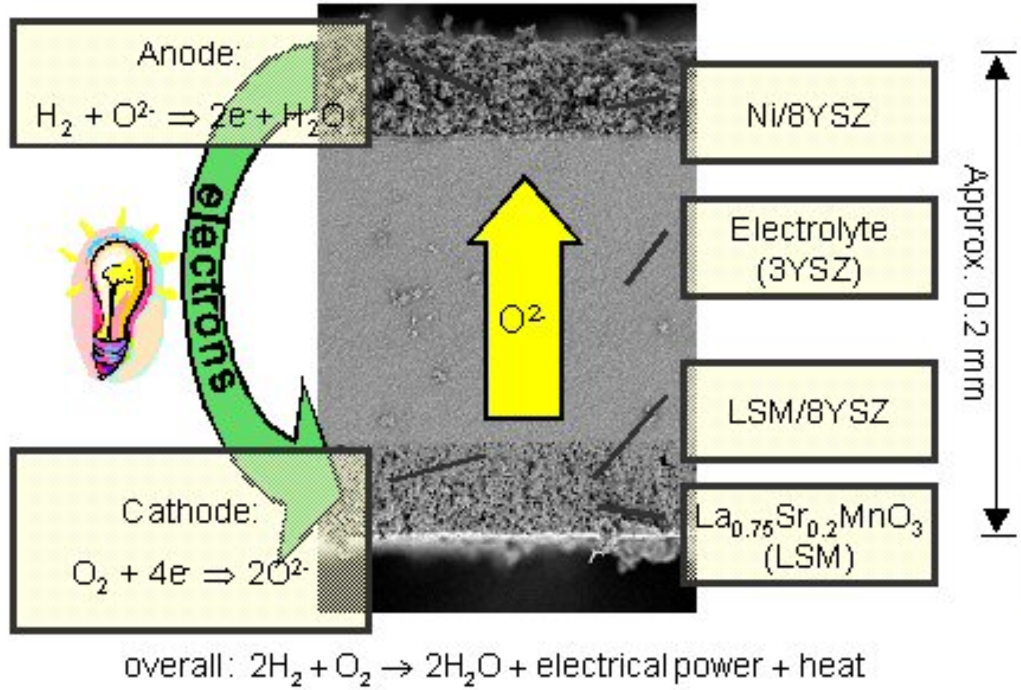

Hydrogen
Anode
Electrolyte
Cathode
Oxygen
Catalyst
Catalyst
H_2
Excess
Hydrogen
(for reuse)
H_2O
Water
Electric
Power

Solid Oxide Fuel Cells (SOFC)

Electrolyte all made up of ceramic substances

- <u>**Anode**</u> : porous carbon
- <u>**Cathode**</u>: Thin porous carbon layer where oxygen reduction occurs.
- Fuel: Hydrogen
- <u>**Electrolyte**</u> : Solid oxide or ceramic electrolyte - Dense layer of oxygen conducting ceramic. - mixture of Ni, ZrO_2 and CaO coated on either side by porous electrode materials. Others include yettrium stabilized zirconia (YSZ) and gadolinium doped ceria (GDC)
- **Operating Temp**: >1000 ^{0}C
- **Efficiency**: 50-60% due to low conductivity solid oxide electrolyte



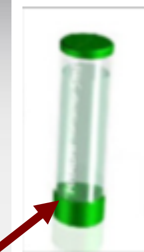


- High efficiency
- Long term stability
- Fuel flexibility
- Low emissions
- High operating temp – longer start up times
- Mechanical / Chemical compatibility issues.

Micro Fuel Cell Powered Small Gadgets

music player

cell phone



fuel cartridge