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CHEMISTRY II

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ELECTROCHEMISTRY II: APPLICATIONS

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Electrolysis: Definition

Electrolysis *is the process in which electrical energy is used to cause a non-spontaneous chemical reaction to occur.*

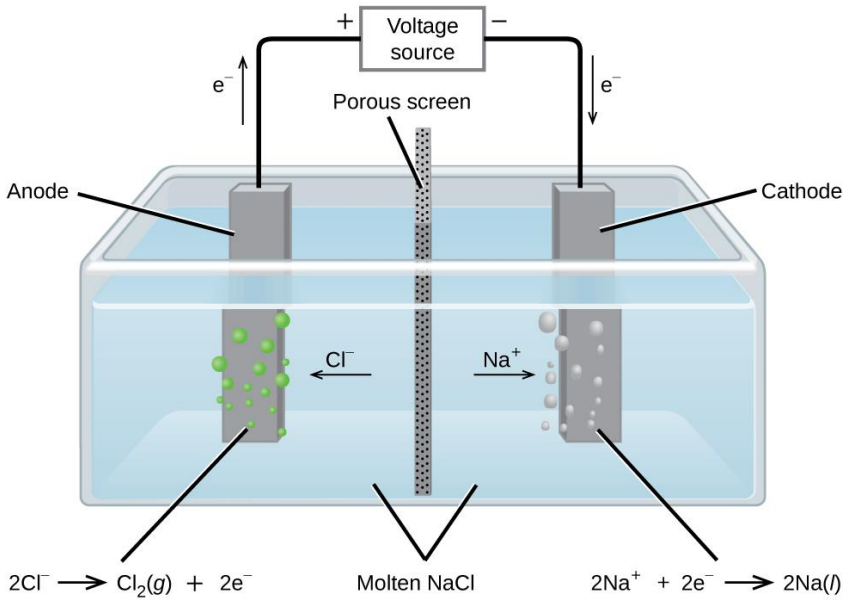
An **Electrolytic cell** is an apparatus for carrying out electrolysis.

Examples of Electrolysis

Electrolysis of Molten Sodium Chloride

In its molten state, sodium chloride, an ionic compound, can be electrolyzed to form sodium metal and chlorine.

Downs cell

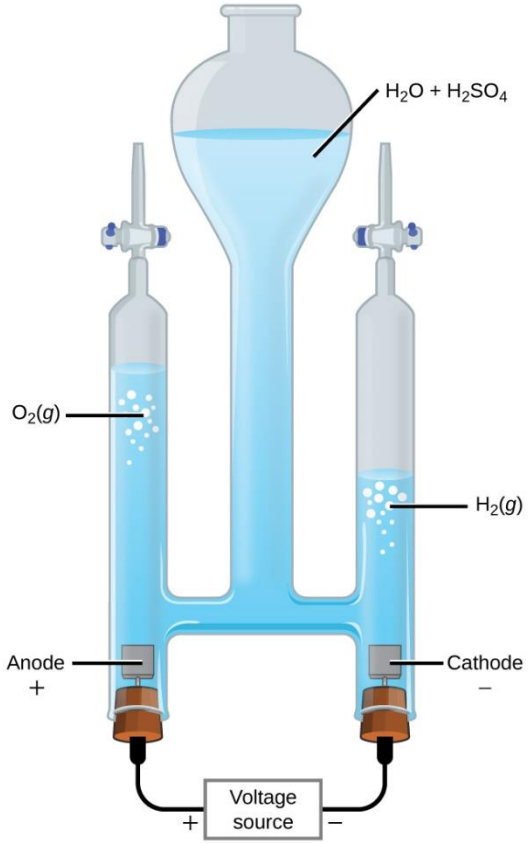


Oxidation
-1.36 V

Reduction
-2.71 V

Examples of Electrolysis

Electrolysis of Water



Water in a beaker under atmospheric conditions (1 atm and 25 ºC) will not spontaneously decompose to form hydrogen and oxygen gas because the standard free energy change for the reaction is a large positive quantity (+474.4 kJ).

The reaction occurs readily in a 0.1 M H_2SO_4 solution:

Anode (Oxidation)

$2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$ $\quad E^o = -1.23\ V$

Cathode (Reduction)

$4\ [H^+\ (aq) + e^- \longrightarrow \frac{1}{2}\ H_2\ (g)]$ $\quad E^o = 0\ V$

Overall reaction

$2H_2O\ (l) \longrightarrow 2H_2\ (g) + O_2\ (g)$ $\quad E^o = -1.23\ V$

Examples of Electrolysis

Electrolysis of an Aqueous Sodium Chloride Solution

Anode (Oxidation)

(1) $2Cl^-$ (aq) ⟶ Cl_2 (g) + $2e^-$ E^o = -1.36 V *By experiment Cl_2 is liberated at the anode*

(2) $2H_2O$ (l) ⟶ O_2 (g) + $4H^+$ (aq) + $4e^-$ E^o = -1.23 V

Cathode (Reduction)

(3) $2H^+$ (aq) + $2e^-$ ⟶ H_2 (g) E^o = 0 V At pH = 7 the concentration of H^+ ions is too low

(4) $2H_2O$ (l) + $2e^-$ ⟶ H_2 (g) + $2OH^-$ (aq) E^o = -0.83 V

(5) Na^+ (aq) + e^- ⟶ Na (s) E^o = -2.71 V A very negative standard reduction potential

Overall reaction

Anode $2Cl^-$ (aq) ⟶ Cl_2 (g) + $2e^-$ E^o = -1.36 V

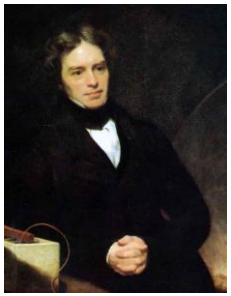
Cathode $2H_2O$ (l) + $2e^-$ ⟶ H_2 (g) + $2OH^-$ (aq) E^o = -0.83 V

Overall $2H_2O$ (l) + $2Cl^-$ (aq) ⟶ H_2 (g) + Cl_2 (g) + $2OH^-$ (aq) E^o = -2.19 V

Hydrogen and chlorine

Basic medium

Quantitative aspects of electrolysis



Michael Faraday
(1791-1867)

Faraday's law: *The mass of product formed (or reactant consumed) at an electrode is proportional to both the amount of electricity transferred at the electrode and the molar mass of the substance in question.*

The **Faraday constant (F)** is the electrical charge contained in one mole of electrons.

$$1 \ mol \ \ e^- = N_A \times q_{e^-} = 6.023 \cdot 10^{23} mol^{-1} \times 1.602 \cdot 10^{-19} C \approx 96500 \ \ C/mol$$

$$\boxed{1 \ \text{Faraday} \ \ (F) = 96500 \ \text{Cmol}^{-1} = 96500 \ \ \text{JV}^{-1}\text{mol}^{-1}}$$

If "**n**" electrons participate in a chemical reaction, "**96500·n**" Coulombs will be needed to produce 1 mol of product.

$$Al^{3+} + 3e^- \rightarrow Al$$

3 mol $e^- \Rightarrow$ 1 mol Al

Steps involved in calculating amounts of substances reduced or oxidized in electrolysis

Electrolysis (t, s)

$$Q = I \times t$$

Current (I, A)

Charge (Q, C)

$$n_e = Q/F$$

Faraday constant (F, C mol^{-1})

Moles of electrons (n_e)

$$n_p = n_e/n^o e^-$$

Number of electrons of the half-reaction

Moles of products (n_p)

$$m_p = n_p \times M$$

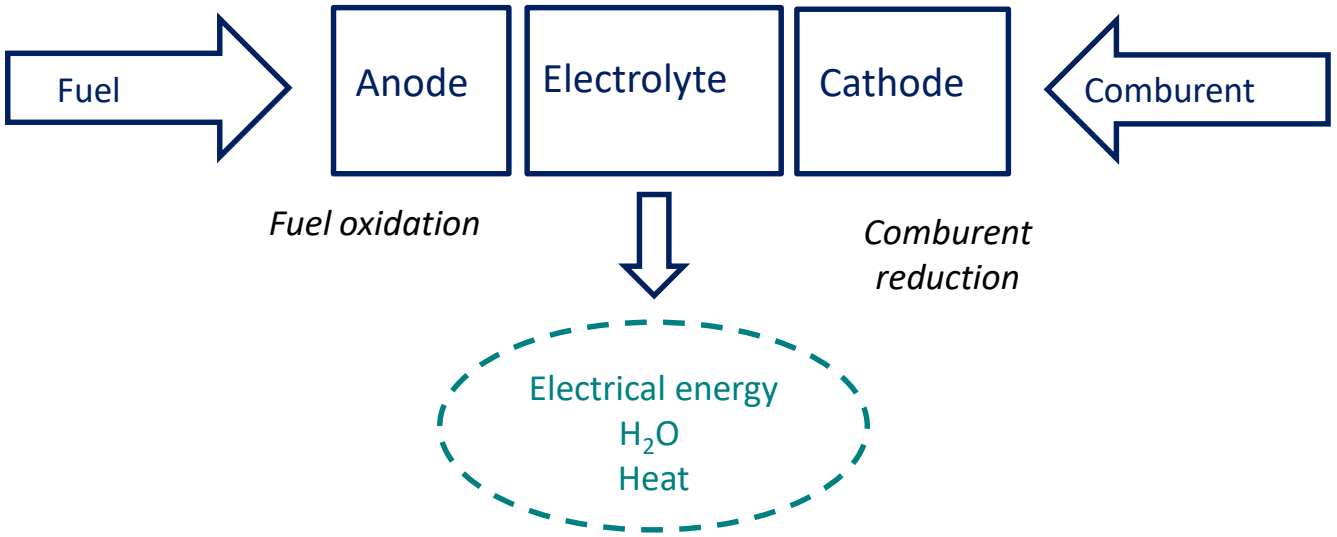
Molecular mass (M)

Grams of product (m_p)

$$m_p = \frac{I \times t \times M}{n^o e^- \times F}$$

Fuel cells: Definition and components

*A **fuel cell** is an electrochemical conversion device that has a continuous supply of fuel such as hydrogen, natural gas, or methanol and an oxidant such as oxygen, air, or hydrogen peroxide. It can have auxiliary parts to feed the device with reactants as well as a battery to supply energy for start-up.*

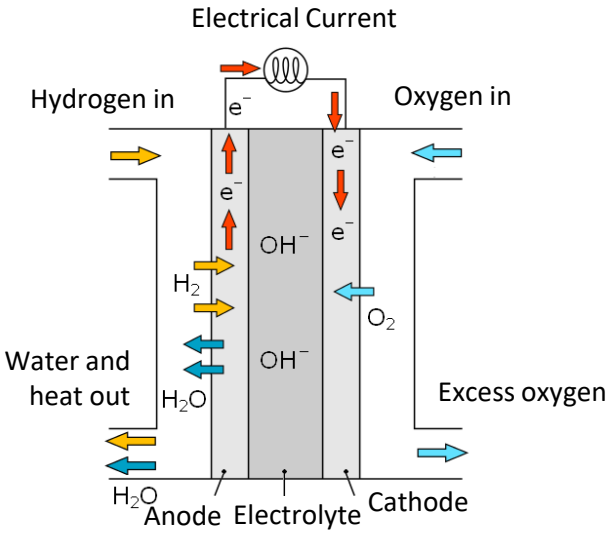


High efficiency
Zero emissions of pollutants (SO_x, NO_x, CO_2 o CO)
High cost

--------> *Eco-friendly*

Alkaline Fuel Cells (AFCs)

*In **AFCs** pure H_2 as fuel and alkaline solutions of potassium hydroxide as electrolytes are used. The operating temperature is about 80 ºC.*



Fuel cell used on the Apollo lunar missions. Museum of the Rockies in Bozeman, Montana

Half-cell reactions

Anode $H_2 + 2OH^- - 2e^- = 2H_2O$

Cathode $O_2 + H_2O + 2e^- = HO_2^- + OH^-$

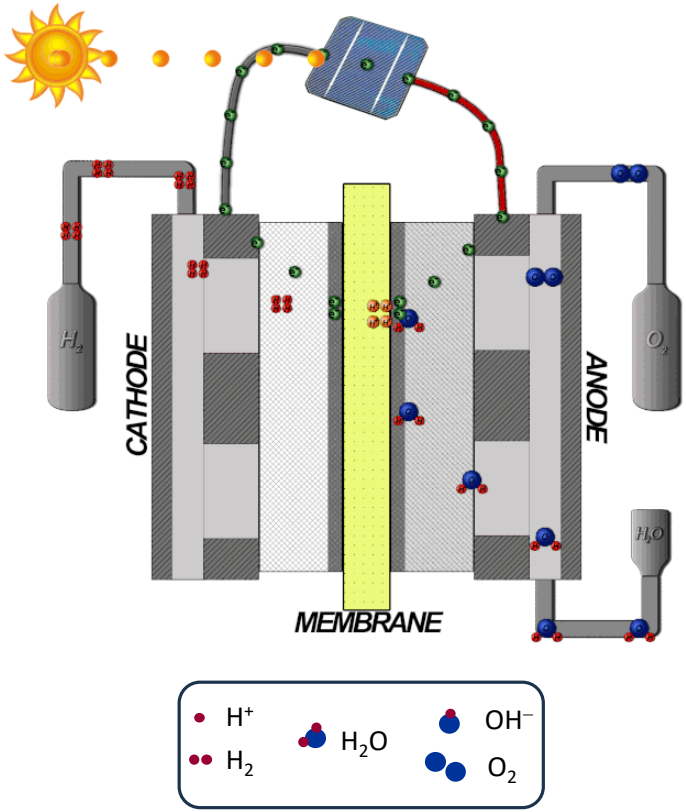
$HO_2^- + H_2O + 2e^- = 3OH^-$

$O_2 + 2H_2O + 4e^- = 4OH^-$

Alkaline electrolytes offer more favorable oxygen reduction kinetics than acid electrolytes.

Polymer Electrolyte Fuel Cells (PEMFCs)

*In a **PEMFC** the electrodes are formed on a thin layer on each side of a proton-conducting polymer membrane, used as electrolyte. The catalyst is typically platinum supported on carbon. Operating temperature is typically between 60 and 80°C.*



$$Cathode \quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$Anode \quad H_2 \rightarrow 2H^+ + 2e^-$$

$$Global\ reaction \quad 2H_2 + O_2 \rightarrow 2H_2O$$

Toyota Mirai Fuel Cell Vehicle

The fuel is contained in high-pressure tanks and fed into a fuel cell stack, where the hydrogen and the oxygen found naturally in the air react with each other and generate electricity.

Direct Methanol Fuel Cells (DMFCs)

*A **DMFC** is essentially a polymer membrane fuel cell that uses metanol instead of hydrogen as a fuel.*

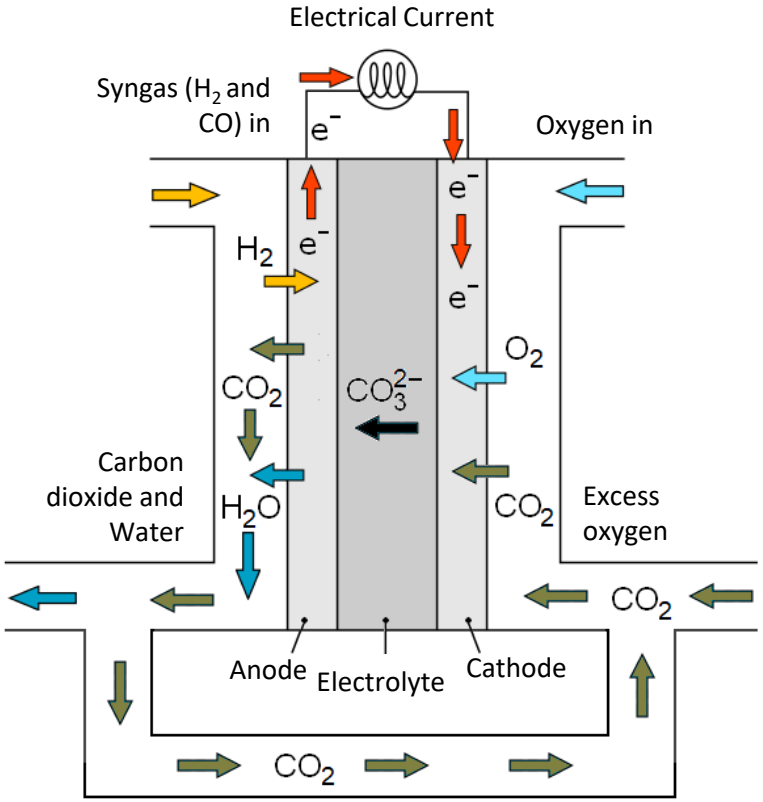
Anode $CH_3OH + H_2O - 6\,e^- \rightarrow 6\,H^+ + CO_2$

Cathode $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

Overall $CH_3OH + {}^3/_2\,O_2 \rightarrow CO_2 + 2\,H_2O \quad E = 1.186\,V$

Molten Carbonate Fuel Cells (MCFCs)

*A **MCFC** has the electrolyte composed of a combination of alkali (Li, Na, K) carbonates, which is retained in a ceramic matrix of $LiAlO_2$. Operating temperatures are between 600 and 700 ºC where the carbonates form a highly conductive molten salt, with carbonates ions providing ionic conduction*



Anode

$CH_4 + 2H_2O = CO_2 + 4H_2$ or

$CH_4 + H_2O = CO + 3H_2$

$CO + H_2O = CO_2 + H_2$

$H_2 + CO_3^{2-} - 2e^- = CO_2 + H_2O$
(principal reaction) or

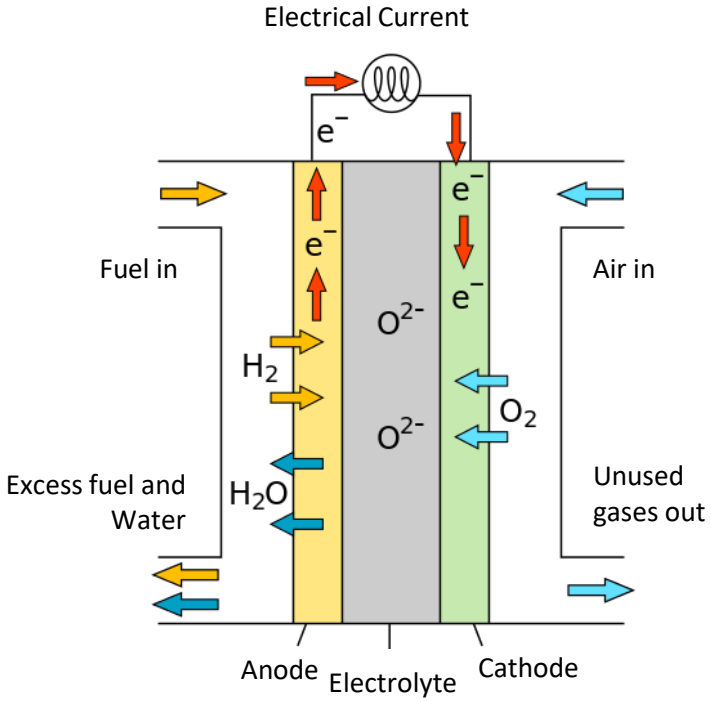
$CO + CO_3^{2-} = 2CO_2$
(minor reaction)

Cathode

$O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$

Solid Oxide Fuel Cells (SOFCs)

*A **SOFC** uses a solid, nonporous metal oxide, usually Y_2O_3-stabilized ZrO_2 (YSZ) as the electrolyte. These cells operate at 800 to 1000 ºC where ionic conduction by oxygen ions (O^{2-}) takes place.*



Cathode

$$O_2 + 4e^- = 2O^{-2}$$

Anode

$$H_2 + O^{2-} - 2e^- = H_2O \text{ or}$$

$$CO + O^{-2} - 2e^- = CO_2 \text{ or}$$

$$CH_4 + 4O^{-2} - 8e^- = 2H_2O + CO_2$$

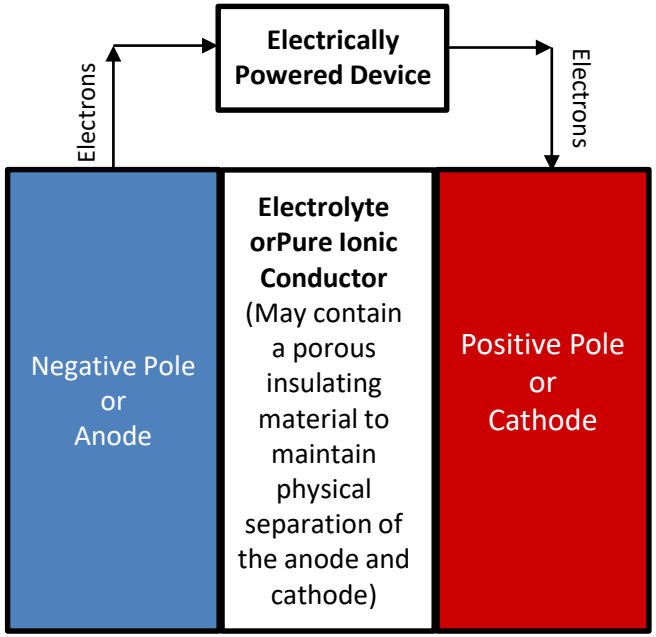
Batteries: Definitions

*A **battery** is an electrochemical cell, or a series of combined electrochemical cells, that can be used as a source of direct electric current at a constant voltage. It is one or more electrically connected electrochemical cells having terminals/contacts to supply electrical energy. Batteries are self-contained units that **store chemical energy** and, on demand, convert it directly into electrical energy to power a variety of applications.*

A **primary battery** is a cell, or group of cells, for the generation of electrical energy intended to be used until exhausted and then discarded. Primary batteries are assembled in the charged state, discharge is the primary process during operation.

A **secondary battery** is a cell or group of cells for the generation of electrical energy in which the cell, after being discharged, may be restored to its original charged condition by an electric current flowing in the direction opposite to the flow of current when the cell was discharged. Other terms for this type of battery are **rechargeable** battery or accumulator. As secondary batteries are usually assembled in the discharged state, they have to be charged first before they can undergo discharge in a secondary process.

Basic elements of a Battery



The negative electrode (**Anode**) is a good reducing agent (electron donor) such as lithium, zinc, or lead.

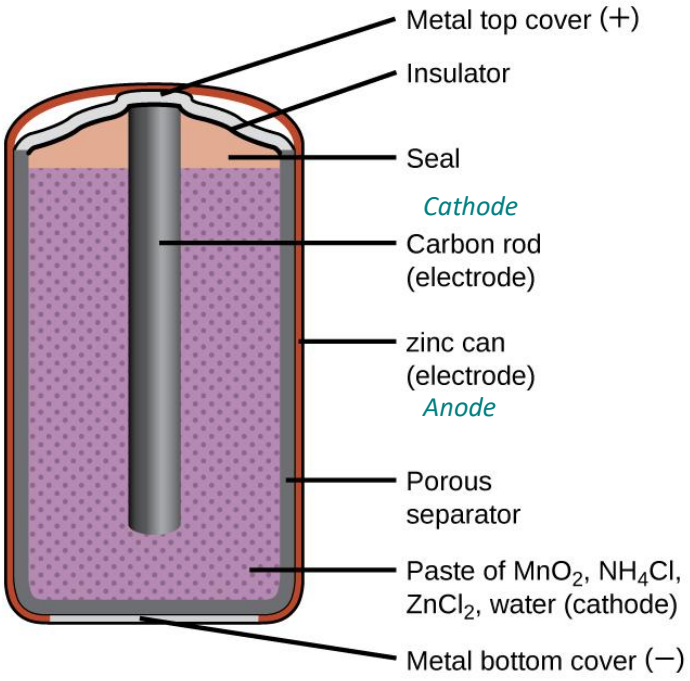
The **electrolyte** is a pure ionic conductor that physically separates the anode from the cathode. They can be subdivided into aqueous, nonaqueous, and solid electrolytes.

The positive electrode (**Cathode**) is an electron acceptor such as lithium, cobalt oxide, manganese, or lead oxide.

Primary Batteries

Leclanché (Carbon-Zinc)

*In the **Lechanché cell** the anode consists of a zinc can or container that is in contact with manganese dioxide (MnO_2) and an electrolyte. The electrolyte consists of ammonium chloride and zinc chloride in water, to which starch is added to thicken the solution to a pastelike consistency so that it is less likely to leak. A carbon rod serves as the cathode, which is immersed in the electrolyte in the center of the cell. It is the most common dry cell, a cell without a fluid component.*



Anode

$$Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$$

Cathode

$$2\ NH_4^+\ (aq) + 2MnO_2\ (s) + 2e^- \longrightarrow Mn_2O_3\ (s) + 2NH_3 + H_2O\ (l)$$

Overall

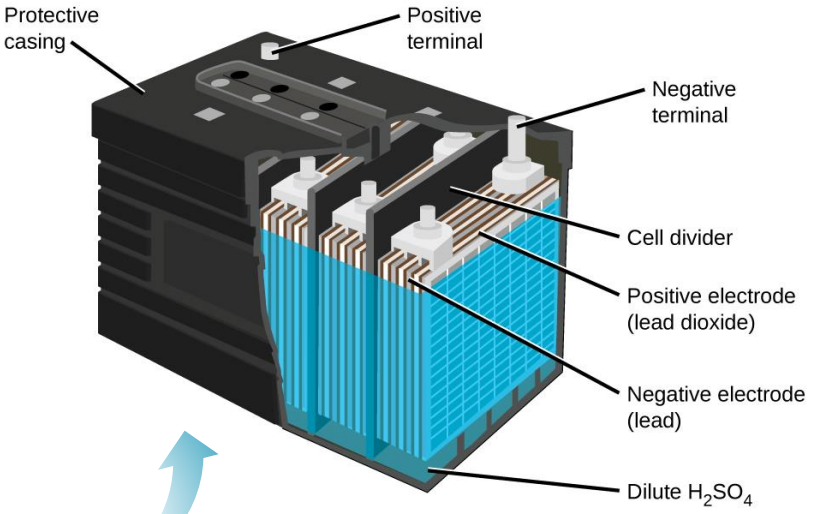
$$Zn\ (s) + 2\ NH_4^+\ (aq) + 2MnO_2\ (s) \longrightarrow Zn^{2+}\ (aq) + Mn_2O_3\ (s) + 2NH_3 + H_2O\ (l)$$

$$E = 1.5\ V$$

Rechargeable Batteries

The Lead Acid Battery

*The **Lead acid battery** consists of six identical cells joined together in series. Each cell has a lead anode and a cathode made of lead dioxide (PbO_2) packed on a metal plate.*



***Discharge**: Both the cathode and the anode are immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte. The cell reactions are:*

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

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

Overall $Pb\ (s) + PbO_2\ (s) + 4\ H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$

Under normal operating conditions, each cell produces 2 V; a total of 12 V from the six cells is used to power the ignition circuit of the automobile and its other electrical systems.

***Charge**: Recharging the battery means reversing the normal electrochemical reaction by applying an external voltage at the cathode and the anode (electrolysis).*

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

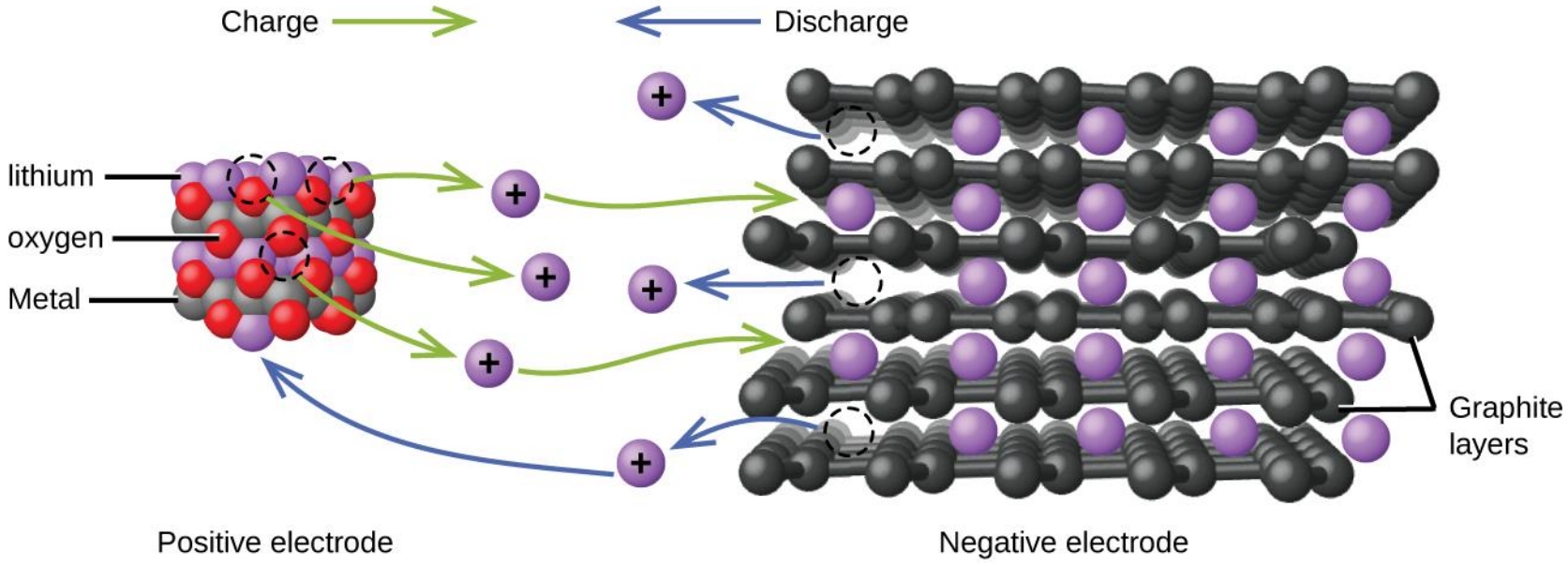
$PbSO_4\ (s) + 2H_2O\ (l) \longrightarrow PbO_2\ (s) + 4\ H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^-$

Overall $2PbSO_4\ (s) + 2H_2O\ (l) \longrightarrow Pb\ (s) + PbO_2\ (s) + 4\ H^+\ (aq) + 2SO_4^{2-}\ (aq)$

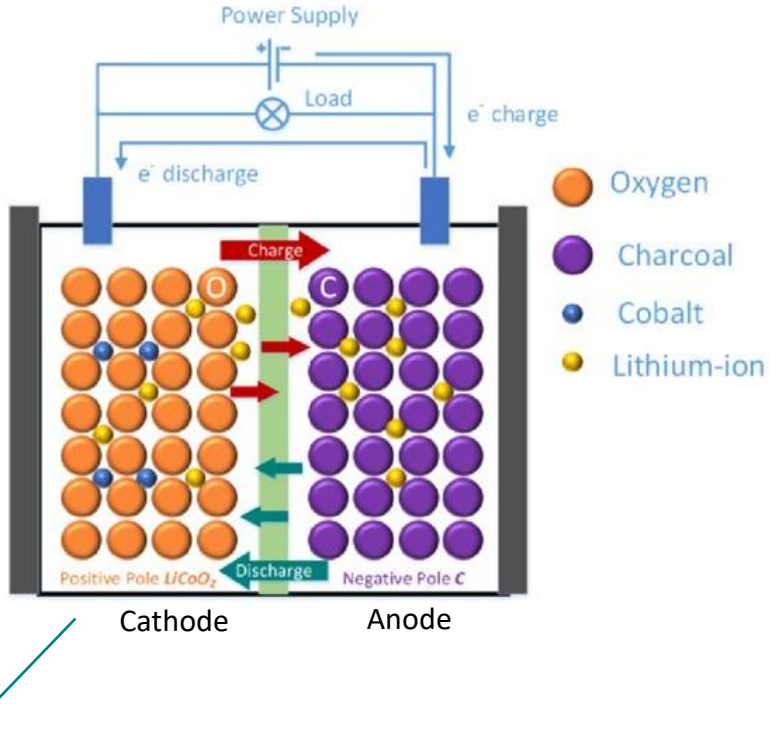
Rechargeable Batteries

The Lithium-Ion battery

*In the **Lithium-ion battery** the anode is made of a conducting carbonaceous material, usually graphite, which has tiny spaces in its structure that can hold both Li atoms and Li^+ ions. The cathode is made of a transition metal oxide such as CoO_2, which can also hold Li^+ ions. Nonaqueous electrolyte (organic solvent + disolved salts) must be used.*



Discharging and Charging reactions



Anode $Li\ (s) \longrightarrow Li^+ + e^-$

Cathode $Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2\ (s)$

Overall $Li\ (s) + CoO_2 \longrightarrow LiCoO_2\ (s) \quad E^o = 3.4\ V$

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