
OpenCourseWare (2023)

CHEMISTRY II

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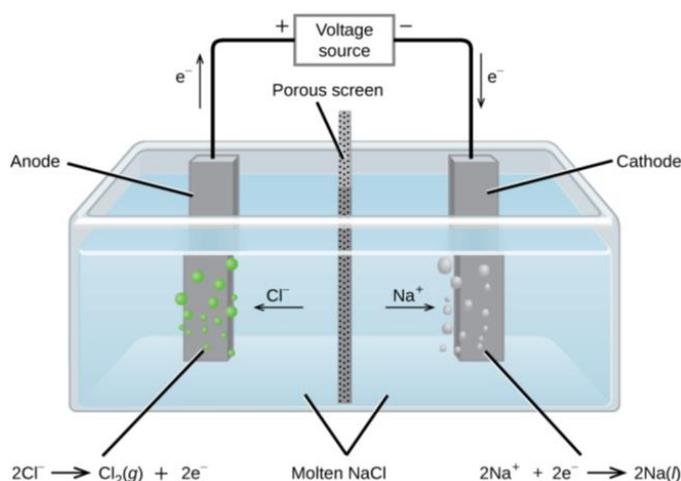
ELECTROCHEMISTRY II



1. ELECTROLYSIS

An electrolytic cell is designed for electrolysis, where the arrangement of components differs from that in galvanic cells. Typically, both electrodes share the same compartment, there is only one electrolyte, and concentrations and pressures result far from standard. In all electrochemical cells, ions carry the current through the electrolyte. Although electrolytic cells differ structurally, an analogy to a galvanic cell helps explain their operation.

In the molten state, sodium chloride, an ionic compound, can undergo electrolysis to produce sodium metal and chlorine. A Downs cell diagram illustrates this process (Figure 1), where the cations and anions are Na^+ and Cl^- , respectively, in molten NaCl . The electrolytic cell features electrodes connected to a battery, serving as an "electron pump," driving electrons to the cathode for reduction and withdrawing electrons from the anode for oxidation. Molten NaCl (melting point $801\text{ }^\circ\text{C}$) forms liquid sodium metal at the cathode, while chlorine gas forms at the anode. The sodium, being lighter, floats to the surface for collection. This process is a significant source of pure sodium metal and chlorine gas. The overall process has an estimated E° value of about -4 V , indicating a nonspontaneous process requiring a minimum of 4 V supplied by the battery.



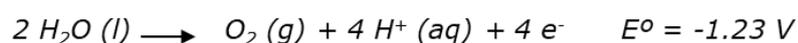
Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, <https://openstax.org/details/books/chemistry-2e>.

Figure 1. Electrolysis of molten sodium chloride.

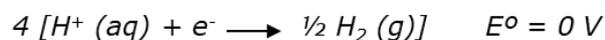
On the other hand, water under atmospheric conditions does not spontaneously decompose into hydrogen and oxygen gas due to a large positive standard free energy change ($+474.4\text{ kJ}$). However, this reaction can be induced in a cell with non-reactive metal electrodes (e.g., platinum) immersed in water. When these electrodes are connected to a battery, nothing occurs initially because pure water lacks sufficient ions to conduct an electric current (at pH 7, the concentration of H^+ is 10^{-7} M , equal to the concentration of OH^-). On the contrary, the reaction readily occurs in a $0.1\text{ M H}_2\text{SO}_4$ solution where there is an ample number of ions to facilitate electricity conduction. Immediately, gas bubbles emerge at both electrodes.

The half-reactions and the overall reaction are outlined, emphasizing that no net H_2SO_4 is consumed. The volume of hydrogen gas produced is twice that of oxygen gas.

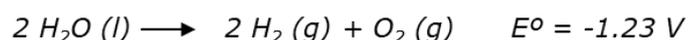
Anode (Oxidation)



Cathode (Reduction)



Overall reaction



The electrolysis of aqueous sodium chloride is more complex. Possible oxidation reactions at the anode include those involving Cl_2 , O_2 , and H_2O . Experimentally, Cl_2 gas is liberated at the anode, defying the expected preference for O_2 formation based on standard reduction potentials. At the cathode, potential reduction reactions involve Cl^- , O_2 , and H_2O , with H_2O being a reasonable choice at a pH of 7. Thus, the electrolysis of aqueous sodium chloride involves complex half-cell reactions, resulting in decreased Cl^- concentrations and increased OH^- concentrations. NaOH , a valuable by-product, can be obtained by evaporating the solution after electrolysis.

2. FARADAY'S LAW

Now, let's explore how to compute the quantity of product formed given a specific number of electrons supplied as an electric current. This calculation is rooted in observations made by Faraday, who stated that the mass of a substance altered (deposited or generated) at an electrode during electrolysis is directly proportional to the quantity of electricity transferred to that electrode. To determine the amount (in moles) of product that an electrical current can form passed for a given time, we must consider the quantity of product that a given number of electrons can form. If n electrons participate in a chemical reaction, $96500n$ coulombs will be needed to produce 1 mol of product. Faraday represents the charge per mole of electrons.

The quantity of electricity, denoted as Q , passing through the electrolysis cell is determined by measuring the current, I , and the time, t , for which the current flows. To establish the number of electrons supplied by a given charge, we use Faraday's constant, F , representing the magnitude of the charge per mole of electrons ($Q = nF$). By combining the number of moles of electrons supplied with the mole ratio derived from the stoichiometry of the electrode reaction, we can deduce the amount of product obtained.

Electrolysis (t , s)		$Q = I \times t$
Charge (Q , C)		$n_e = Q/F$
Moles of electrons (n_e)		$n_p = n_e / n^\circ e^-$
Moles of products (n_p)		$m_p = n_p \times M$
Grams of product (m_p)		$m_p = \frac{I \times t \times M}{n^\circ e^- \times F}$

3. FUEL CELLS: TYPES AND APPLICATIONS

In batteries and fuel cells, electrical energy is generated through the conversion of chemical energy via redox reactions occurring at the anode and cathode. As reactions at the anode typically take place at lower electrode potentials than at the cathode, terms like negative and positive electrodes (indicated as minus and plus poles) are employed. The more negative electrode is termed the anode, while the cathode is the more positive. The distinction between batteries and fuel cells lies in energy storage and conversion locations.

A fuel cell, functioning as an electrochemical cell, requires a continuous supply of reactants to operate. It is a conversion device with a steady fuel supply, such as hydrogen, natural gas, or methanol, and an oxidant, such as oxygen, air, or hydrogen peroxide. Fuel cells are equipped with auxiliary parts to feed reactants and, at times, a battery for start-up energy. They typically consist of an anode (where oxidation occurs), a cathode (where reduction occurs), and an electrolyte (where ions carry the current between the electrodes). Unlike batteries, fuel and oxidants are continuously supplied from an external source. While fuel cells operate as long as the fuel is supplied, they are not electrically recharged. The fuel of choice is often hydrogen gas, producing water as an exhaust gas. Other fuels and hydrocarbons may need conversion to hydrogen for fuel cell use.

Fuel cells, functioning as electrical devices, directly convert chemical energy into electrical energy and heat and emit low or zero pollutant emissions. They come in various types based on the electrolyte, including alkaline fuel cells (AFC), polymer electrolyte fuel cells (PEMFC), phosphoric acid fuel cells (PAFC), and molten carbonate fuel cells (MCFC).

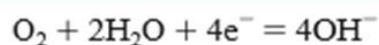
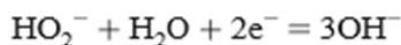
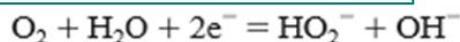
Alkaline Fuel Cells (AFC) use pure H_2 as fuel and alkaline potassium hydroxide solutions as electrolytes. They operate at around $80^\circ C$, offering favorable oxygen reduction kinetics.

Half-cell reactions

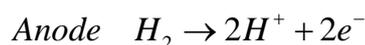
Anode



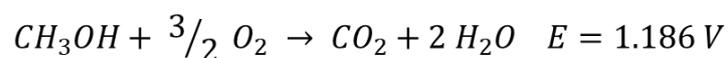
Cathode



Polymer Electrolyte Fuel Cells (PEMFC) use a thin proton-conductive polymer membrane as the electrolyte, operating at temperatures between 60 and 80 °C. PEMFC employs a slender (<50µm) proton-conductive polymer membrane, such as perfluorosulfonated acid polymer, as the electrolyte. The catalyst, usually platinum supported on carbon with loadings of approximately 0.3 mg/cm², is used. In cases where the hydrogen feed contains trace amounts of CO, Pt-Ru alloys are employed. Operating at temperatures typically between 60 and 80 °C, PEM fuel cells are a promising solution for automotive applications, small-scale distributed stationary power generation, and portable power applications.



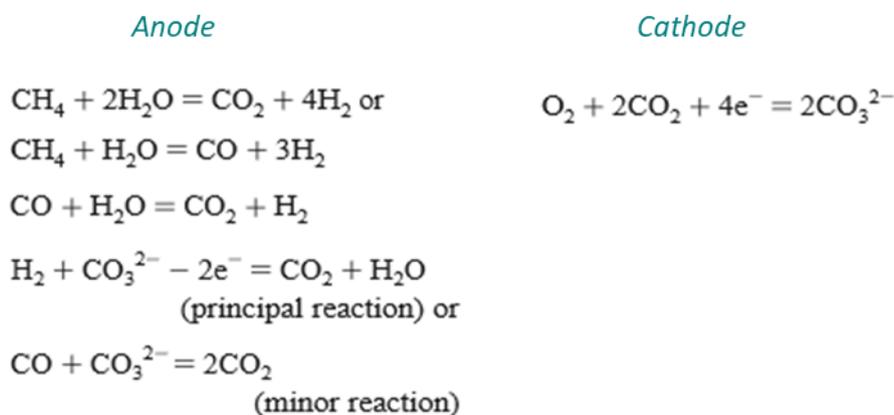
The *Direct Methanol Fuel Cell* (DMFC) is often classified as a distinct type of fuel cell, yet, based on the previous categorization relying on electrolyte composition, it essentially functions as a polymer membrane fuel cell utilizing methanol instead of hydrogen as its primary fuel. Operating on the same fundamental cell architecture as the PEMFC, the DMFC boasts the advantage of a liquid fuel, facilitating easy storage and transport. Unlike other fuel cells, it eliminates the need for a reformer to convert hydrocarbon fuel into hydrogen gas. Depending on the specific cell configuration, the anode feedstock involves a methanol and water mixture or neat methanol.



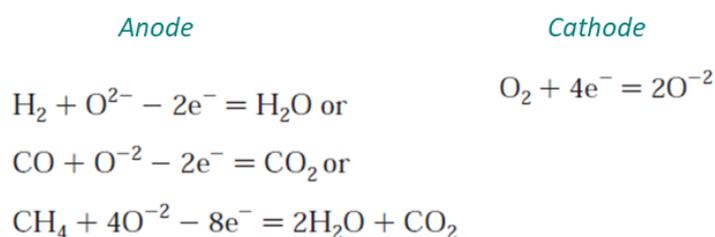
Currently under development, the DMFC shows promise as a power source for portable electronic devices such as notebook computers and cellular phones. The anode catalyst loadings, particularly platinum-ruthenium, are higher than the PEMFC, ranging from 1-3 mg/cm². The absence of ruthenium leads to the production of a stable formic acid intermediate during the anode reaction. The direct conversion of methanol exhibits a voltage comparable to hydrogen. However, the chemical similarity between water and methanol results in a significant crossover, reducing the cathode voltage and overall cell efficiency. Typically, a DMFC yields around 0.5 V at 400 mA/cm² at 60 °C.

Molten carbonate fuel cells (MCFC) employ an electrolyte composed of alkali carbonates (Li, Na, K) retained in a ceramic matrix of LiAlO₂. Operating at temperatures between 600 and 700 °C, the carbonates form a highly conductive molten salt, obviating the need for noble metal catalysts. Currently, in the precommercial/demonstration stage for stationary power generation, MCFCs have applications in energy

storage, operating optimally at ~ 560 °C. Unlike other fuel cell types, they do not require noble metal catalysts, showcasing higher efficiency than PEMFCs and PAFCs. The LiAlO_2 ceramic tile separator, filled with molten carbonates, prevents reactant crossover and aids in CO_3^{2-} transport. Challenges at the operating temperature include NiO dissolution, structural stability issues in anodes and cathodes, and control of pore diameter in separator tiles.



Solid oxide fuel cells (SOFC) utilize a solid, nonporous metal oxide, usually Y_2O_3 -stabilized ZrO_2 (YSZ), as the electrolyte. Operating at 800 to 1000 °C, these fuel cells are in the precommercial/demonstration stage for stationary power generation, with smaller units in development for portable and auxiliary power in automobiles. With O_2 -conduction in the solid phase, SOFCs overcome challenges posed by high operating temperatures, achieving close to 96% thermodynamic efficiency. The absence of noble metal catalysts and the ability to operate on various hydrocarbon or hydrogen fuels makes SOFCs versatile. The anode consists of a porous cermet of Ni or Co catalyst on YSZ, while the cathode is typically a strontia-doped lanthanum-manganite perovskite. Cells are constructed in cylindrical or flat plate formats.



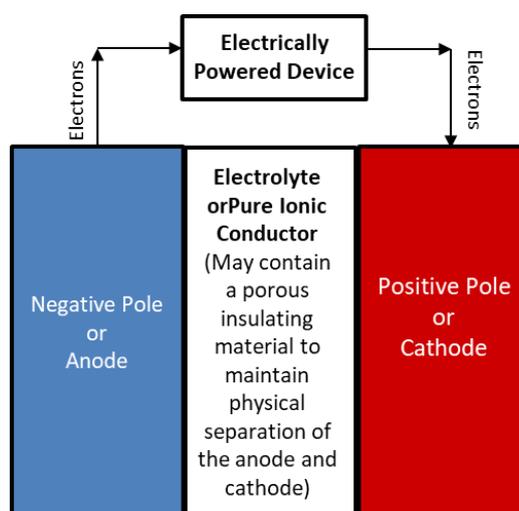
4. BATTERIES: TYPES AND APPLICATIONS

A battery serves as an electrochemical cell or a combination of such cells, capable of providing a steady supply of direct electric current at a constant voltage. It comprises one or more electrically connected electrochemical cells equipped with terminals/contacts to deliver electrical energy. Batteries, self-contained units, store chemical energy and promptly convert it into electrical energy upon demand to power diverse applications.

A **primary battery** is a cell or a group of cells designed to generate electrical energy, intended to be utilized until fully depleted and disposed of. These batteries are assembled in a charged state, with discharge being the primary process during operation. On the other hand, a **secondary battery** is a cell or

group of cells intended to generate electrical energy. After discharge, it can be restored to its original charged condition by applying an electric current opposite to the flow during discharge. Also known as rechargeable batteries or accumulators, secondary batteries are typically assembled in a discharged state and must be charged before undergoing a secondary discharge process.

The Figure 2 depicting the fundamental components illustrates the operation of the battery. It showcases the energy levels at the anode (negative) and cathode (positive) poles as well as the electrolyte, expressed in electronvolts. The negative electrode serves as a good reducing agent (electron donor), such as lithium, zinc, or lead. In contrast, the positive electrode acts as an electron acceptor, incorporating materials like lithium cobalt oxide, manganese dioxide, or lead oxide. The electrolyte, a pure ionic conductor, physically separates the anode from the cathode.



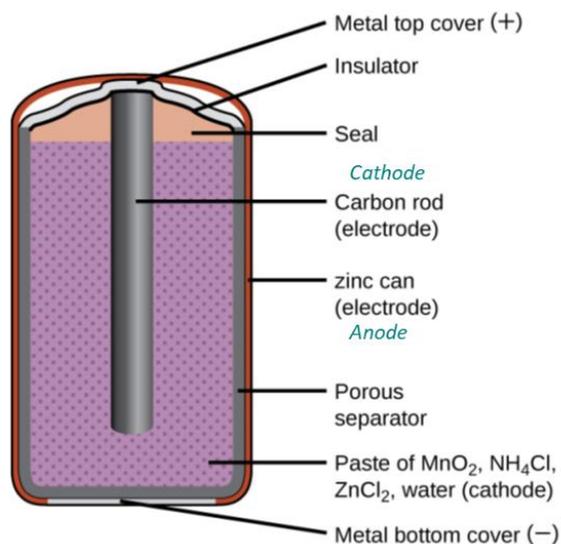
Source: Image made by the authors.

Figure 2. Basic elements of a battery.

Battery electrolytes typically come in liquid solvent form and can be categorized as aqueous, nonaqueous, or solid. Aqueous electrolytes are typically salts of strong acids and bases, completely dissociating into positive and negative ions in solution. The electrolyte facilitates ionic conduction and physically separates the positive and negative electrodes for proper electrochemical cell function. However, each electrolyte has a specific stability range, and exceeding this range leads to decomposition. The voltage stability window depends on the composition and purity of the electrolyte.

Standard commercial systems include primary batteries, assembled in a charged state for single-use until exhaustion; secondary batteries, rechargeable and assembled in a discharged state, requiring charging before secondary discharge; and specialty batteries, limited in production for specific end-use applications.

Zinc-manganese batteries currently dominate the primary battery market segment, with the original carbon-zinc cell invented by Leclanché in 1860. Leclanché's cell utilized a natural manganese dioxide-carbon black core cathode and an aqueous zinc chloride-ammonium chloride electrolyte housed in a zinc can (Figure 3). An improved version employs a zinc chloride electrolyte and synthetic electrolytic manganese dioxide, demonstrating superior performance to the original Leclanché cell.



Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, <https://openstax.org/details/books/chemistry-2e>.

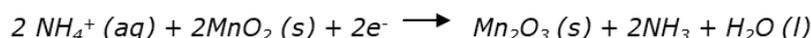
Figure 3. Electrolysis of molten sodium chloride.

Zinc-manganese batteries incorporate MnO_2 as a proton insertion cathode and a Zn anode of the solution type. Depending on its pH, the dissolution or precipitation of Zn^{2+} cations in the electrolyte characterizes the discharge mechanism. The MnO_2 electrode undergoes a two-step one-electron reduction during discharge, starting at cell voltages of 1.5 V.

Anode



Cathode



Overall

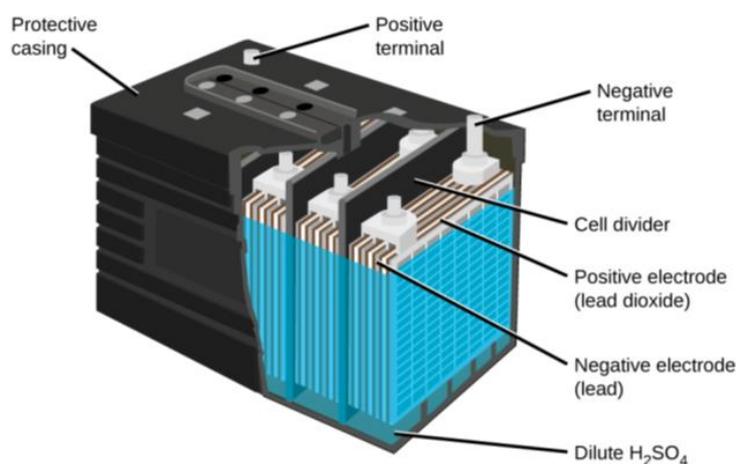


$$E = 1.5 V$$

Rechargeable cells typically exhibit lower energy storage capacity than primary cells due to additional requirements for recharging and prolonged operation. The lead-acid battery dominates the rechargeable market, characterized by lead and lead oxide electrodes requiring sulfuric acid and water for cell reaction and electrolyte formation. Despite the practical value of specific energy being only 25% of the theoretical one due to components like grids, separators, and cell containers, the lead-acid system finds extensive use in applications ranging from automotive SLI (starting, lighting, and ignition) to stationary energy storage. Its low cost and effective recycling processes contribute to its environmental sustainability.

The lead acid battery comprises six identical cells connected in series, each featuring a lead anode and a lead dioxide (PbO_2) cathode on a metal plate (Figure 4). Discharge involves immersion in an aqueous

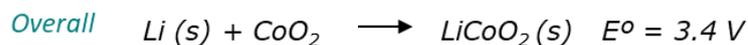
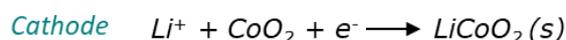
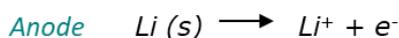
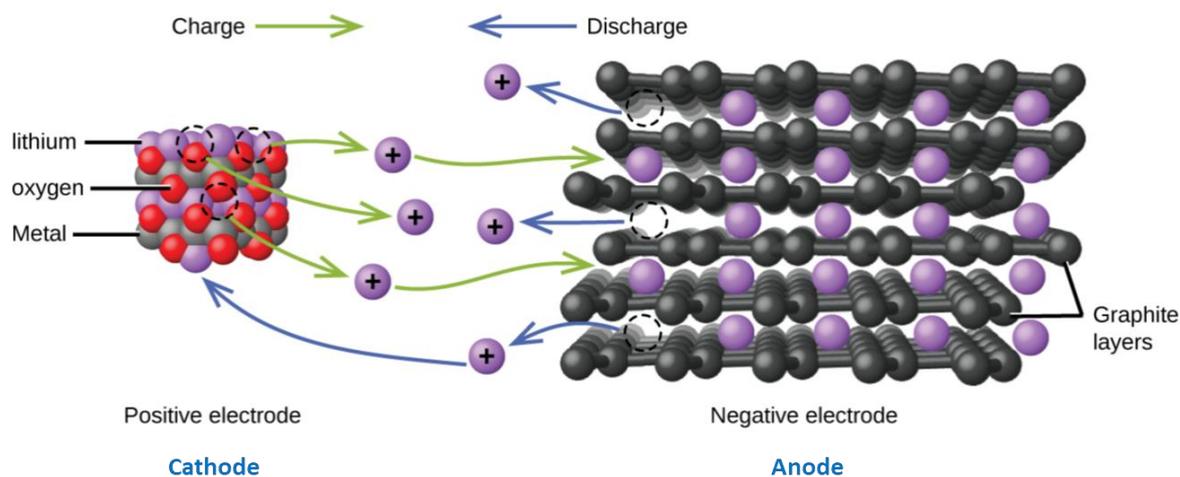
sulfuric acid solution, leading to cell reactions that produce a total of 12 V from the six cells, powering the vehicle's ignition circuit and other electrical systems. The lead storage battery delivers large currents for short durations, making it ideal for engine startup.



Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, <https://openstax.org/details/books/chemistry-2e>.

Figure 4. Lead acid battery.

In contrast, with higher energy density and lighter weight, the *lithium-ion battery* replaced Ni-MH batteries as soon as production capabilities allowed. It is now the preferred battery for portable electronic devices. Figure 5 illustrated the Li-ion cell, which typically consists of a carbon/graphite anode, a lithium-cobalt oxide cathode, and an organic electrolyte of lithium hexafluorophosphate (LiPF_6) salt with an ethylene carbonate-organic solvent mixture.



Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, <https://openstax.org/details/books/chemistry-2e>.

Figure 5. Lithium-ion battery.

The Li-ion battery's anode, typically graphite, contains tiny spaces capable of holding Li atoms and ions. The cathode, made of a transition metal oxide like CoO_2 , also accommodates Li^+ ions. A nonaqueous electrolyte (organic solvent + dissolved salts) is necessary due to the high reactivity of the metal. Discharge reactions involve lithium ions moving from the anode to the cathode. The advantage lies in lithium's highly negative standard reduction potential and lightweight nature, allowing Li-ion batteries to be recharged hundreds of times without deterioration. These batteries boast high energy density, no memory effect (except for lithium iron phosphate cells), and low self-discharge. However, safety concerns arise from the flammable electrolyte, leading to incidents like the Samsung Galaxy Note 7 recall and battery issues on Boeing 787s.