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Electrolysis

In chemistry and manufacturing, **electrolysis** is a technique that uses direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially important as a stage in the separation of <u>elements</u> from naturally occurring sources such as <u>ores</u> using an <u>electrolytic cell</u>. The <u>voltage</u> that is needed for electrolysis to occur is called the decomposition potential. The word "lysis" means to separate or break, so in terms, electrolysis would mean "breakdown via electricity".

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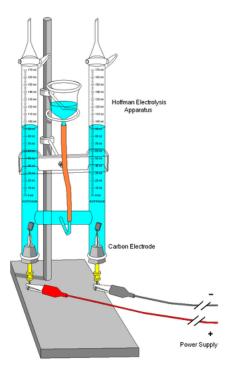


Illustration of a <u>Hofmann electrolysis</u> <u>apparatus</u> used in a school laboratory The word "electrolysis" was introduced by <u>Michael Faraday</u> in 1834,^[1] using the <u>Greek</u> words $\ddot{\eta}\lambda\epsilon\kappa\tau\rho\sigma\nu$ [$\check{\epsilon}$:lektron] "amber", which since the 17th century was associated with <u>electrical</u> <u>phenomena</u>, and $\lambda\dot{\upsilon}\sigma\iota\varsigma$ [lýsis] meaning "dissolution". Nevertheless, electrolysis, as a tool to study chemical reactions and obtain pure <u>elements</u>, precedes the coinage of the term and formal description by Faraday.

History

In the early nineteenth century, <u>William Nicholson</u> and <u>Anthony Carlisle</u> sought to further <u>Volta's</u> experiments. They attached two wires to either side of a <u>voltaic pile</u> and placed the other ends in a tube filled with water. They noticed when the wires were brought together that each wire produced bubbles. One type was hydrogen, the other was oxygen.^[2]

In 1785 a Dutch scientist named <u>Martin van Marum</u> created an electrostatic generator that he used to reduce tin, zinc and antimony from their salts using a process later known as electrolysis. Though he unknowingly produced electrolysis, it was not until 1800 when William Nicholson and Anthony Carlisle discovered how electrolysis works.^[3]

In 1791 <u>Luigi Galvani</u> experimented with frog legs. He claimed that placing animal muscle between two dissimilar metal sheets resulted in electricity. Responding to these claims, <u>Alessandro Volta</u> conducted his own tests.^{[4][5]} This would give insight to <u>Humphry Davy</u>'s ideas on electrolysis. During preliminary experiments, Humphry Davy hypothesized that when two elements combine together to form a compound, electrical energy is released. Humphry Davy would go on to create Decomposition Tables from his preliminary experiments on Electrolysis. The Decomposition Tables would give insight on the energies needed to break apart certain compounds.^[6]

In 1817 Johan August Arfwedson determined there was another element, lithium, in some of his samples; however, he could not isolate the component. It was not until 1821 when <u>William Thomas</u> <u>Brande</u> used electrolysis to single it out. Two years later, he streamlined the process using lithium chloride and potassium chloride with electrolysis to produce lithium and lithium hydroxide.^{[7][8]}

During the later years of Humphry Davy's research, Michael Faraday became his assistant. While studying the process of electrolysis under Humphry Davy, Michael Faraday discovered two <u>laws of</u> electrolysis.^[5]

During the time of Maxwell and Faraday, concerns came about for <u>electropositive</u> and <u>electronegative</u> activities.^[9]

In November 1875, <u>Paul Émile Lecoq de Boisbaudran</u> discovered <u>gallium</u> using electrolysis of gallium hydroxide, producing 3.4 mg of gallium. The following December, he presented his discovery of gallium to the <u>Académie des sciences</u> in Paris.^[10]

On June 26, 1886, <u>Ferdinand Frederick Henri Moissan</u> finally felt comfortable performing electrolysis on <u>anhydrous</u> hydrogen fluoride to create a gaseous fluorine pure element. Before he used hydrogen fluoride, Henri Moissan used fluoride salts with electrolysis. Thus on June 28, 1886, he performed his experiment in front of the Académie des sciences to show his discovery of the new element fluorine.^[11] While trying to find elemental fluorine through electrolysis of fluoride salts, many chemists perished including Paulin Louyet and Jérôme Nicklès.^[12]

In 1886 <u>Charles Martin Hall</u> from America and <u>Paul Héroult</u> from France both filed for American patents for the electrolysis of aluminum, with Héroult submitting his in May, and Hall, in July.^[13] Hall was able to get his patent by proving through letters to his brother and family evidence that his method was discovered before the French patent was submitted.^[14] This became known as the <u>Hall-Héroult</u> process which benefited many industries because aluminum's price then dropped from four dollars to thirty cents per pound.^[15]

Timeline

- 1785 Martinus van Marum's electrostatic generator was used to reduce tin, zinc, and antimony from their salts using electrolysis.^[16]
- 1800 William Nicholson and Anthony Carlisle (and also Johann Ritter), decomposed water into hydrogen and oxygen.
- 1808 Potassium (1807), sodium (1807), barium, calcium and magnesium were discovered by Humphry Davy using electrolysis.
- 1821 Lithium was discovered by the English chemist William Thomas Brande, who obtained it by electrolysis of lithium oxide.
- 1834 Michael Faraday published his two laws of electrolysis, provided a mathematical explanation for them, and introduced terminology such as electrode, electrolyte, anode, cathode, anion, and cation.
- 1875 Paul Émile Lecoq de Boisbaudran discovered gallium using electrolysis.^[17]
- 1886 Fluorine was discovered by Henri Moissan using electrolysis.
- 1886 Hall–Héroult process developed for making aluminium
- 1890 Castner–Kellner process developed for making sodium hydroxide.

Overview

Electrolysis is the passing of a <u>direct electric current</u> through an <u>electrolyte</u> producing chemical reactions at the <u>electrodes</u> and <u>decomposition</u> of the materials.

The main components required to achieve electrolysis are an <u>electrolyte</u>, electrodes, and an external power source. A partition (e.g. an <u>ion-exchange membrane</u> or a <u>salt bridge</u>) is optional to keep the products from diffusing to the vicinity of the opposite electrode.

The electrolyte is a <u>chemical substance</u> which contains <u>free ions</u> and <u>carries electric current</u> (e.g. an ion-conducting <u>polymer</u>, solution, or a <u>ionic liquid</u> compound). If the ions are not mobile, as in most solid <u>salts</u>, then electrolysis cannot occur. A liquid electrolyte is produced by:

- <u>Solvation</u> or reaction of an <u>ionic compound</u> with a <u>solvent</u> (such as water) to produce mobile ions
- An ionic compound melted by heating

The electrodes are immersed separated by a distance such that a current flows between them through the electrolyte and are connected to the power source which completes the <u>electrical</u> <u>circuit</u>. A <u>direct current</u> supplied by the power source drives the reaction causing ions in the electrolyte to be attracted toward the respective oppositely charged electrode.

Electrodes of <u>metal</u>, <u>graphite</u> and <u>semiconductor</u> material are widely used. Choice of suitable <u>electrode</u> depends on chemical reactivity between the electrode and electrolyte and manufacturing cost. Historically, when non-reactive anodes were desired for electrolysis, graphite (called plumbago in Faraday's time) or platinum were chosen.^[18] They were found to be some of the least reactive materials for anodes. Platinum erodes very slowly compared to other materials, and graphite crumbles and can produce carbon dioxide in aqueous solutions but otherwise does not participate in the reaction. Cathodes may be made of the same material, or they may be made from a more reactive one since anode wear is greater due to oxidation at the anode.

Process of electrolysis

The key process of electrolysis is the interchange of atoms and ions by the removal or addition of electrons due to the applied current. The desired products of electrolysis are often in a different physical state from the electrolyte and can be removed by mechanical processes (e.g. by collecting gas above an electrode or precipitating a product out of the electrolyte).

The quantity of the products is proportional to the current, and when two or more electrolytic cells are connected in series to the same power source, the products produced in the cells are proportional to their equivalent weight. These are known as Faraday's laws of electrolysis.

Each electrode attracts ions that are of the opposite <u>charge</u>. Positively charged ions (<u>cations</u>) move towards the electron-providing (negative) cathode. Negatively charged ions (<u>anions</u>) move towards the electron-extracting (positive) anode. In this process <u>electrons</u> are effectively introduced at the cathode as a <u>reactant</u> and removed at the anode as a <u>product</u>. In chemistry, the loss of electrons is called oxidation, while electron gain is called reduction.

When neutral atoms or molecules, such as those on the surface of an electrode, gain or lose electrons they become ions and may dissolve in the electrolyte and react with other ions.

When ions gain or lose electrons and become neutral, they will form compounds that separate from the electrolyte. Positive metal ions like Cu²⁺ deposit onto the cathode in a layer. The terms for this are electroplating, electrowinning, and electrorefining.

When an ion gains or loses electrons without becoming neutral, its electronic charge is altered in the process.

For example, the <u>electrolysis of brine</u> produces hydrogen and chlorine gases which bubble from the electrolyte and are collected. The initial overall reaction is thus:^[19]

$$2 \text{ NaCl} + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ NaOH} + \text{H}_2 + \text{Cl}_2$$

The reaction at the anode results in chlorine gas from chlorine ions:

 $2 \text{ Cl}^- \rightarrow \text{Cl}_2 + 2 \text{ e}^-$

The reaction at the cathode results in hydrogen gas and hydroxide ions:

 $2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$

Without a partition between the electrodes, the OH^- ions produced at the cathode are free to diffuse throughout the electrolyte to the anode. As the electrolyte becomes more <u>basic</u> due to the production of OH^- , less Cl_2 emerges from the solution as it begins to react with the hydroxide producing hypochlorite (ClO⁻) at the anode:

 $Cl_2 + 2 NaOH \rightarrow NaCI + NaCIO + H_2O$

The more opportunity the Cl_2 has to interact with NaOH in the solution, the less Cl_2 emerges at the surface of the solution and the faster the production of hypochlorite progresses. This depends on factors such as solution temperature, the amount of time the Cl_2 molecule is in contact with the solution, and concentration of NaOH.

Likewise, as hypochlorite increases in concentration, chlorates are produced from them:

 $3 \text{ NaClO} \rightarrow \text{NaClO}_3 + 2 \text{ NaCl}$

Other reactions occur, such as the <u>self-ionization of water</u> and the decomposition of hypochlorite at the cathode, the rate of the latter depends on factors such as <u>diffusion</u> and the surface area of the cathode in contact with the electrolyte.^[20]

Decomposition potential

Decomposition potential or decomposition voltage refers to the minimum voltage (difference in <u>electrode potential</u>) between <u>anode</u> and <u>cathode</u> of an electrolytic cell that is needed for electrolysis to occur.^[21]

The voltage at which electrolysis is thermodynamically preferred is the difference of the electrode potentials as calculated using the <u>Nernst equation</u>. Applying additional voltage, referred to as <u>overpotential</u>, can increase the rate of reaction and is often needed above the thermodynamic value. It is especially necessary for electrolysis reactions involving gases, such as <u>oxygen</u>, <u>hydrogen</u> or chlorine.

Oxidation and reduction at the electrodes

<u>Oxidation</u> of ions or neutral molecules occurs at the <u>anode</u>. For example, it is possible to oxidize ferrous ions to ferric ions at the anode:

$$\mathrm{Fe}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^{-}$$

<u>Reduction</u> of ions or neutral molecules occurs at the <u>cathode</u>. It is possible to reduce <u>ferricyanide</u> ions to <u>ferrocyanide</u> ions at the cathode:

$$\mathrm{Fe}(\mathrm{CN})_{6}^{3\text{-}} + \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{CN})_{6}^{4\text{-}}$$

Neutral molecules can also react at either of the electrodes. For example: p-benzoquinone can be

reduced to hydroquinone at the cathode:

$$+ 2 e^{-} + 2 H^{+} \rightarrow HO - -OH$$

In the last example, H^+ ions (hydrogen ions) also take part in the reaction and are provided by the acid in the solution, or by the solvent itself (water, methanol, etc.). Electrolysis reactions involving H^+ ions are fairly common in acidic solutions. In aqueous alkaline solutions, reactions involving OH^- (hydroxide ions) are common.

Sometimes the solvents themselves (usually water) are oxidized or reduced at the electrodes. It is even possible to have electrolysis involving gases, e.g. by using a gas diffusion electrode.

Energy changes during electrolysis

The amount of electrical energy that must be added equals the change in <u>Gibbs free energy</u> of the reaction plus the losses in the system. The losses can (in theory) be arbitrarily close to zero, so the maximum <u>thermodynamic</u> efficiency equals the <u>enthalpy</u> change divided by the free energy change of the reaction. In most cases, the electric input is larger than the enthalpy change of the reaction, so some energy is released in the form of heat. In some cases, for instance, in the electrolysis of <u>steam</u> into hydrogen and oxygen at high temperature, the opposite is true and heat energy is absorbed. This heat is absorbed from the surroundings, and the <u>heating value</u> of the produced hydrogen is higher than the electric input.

Variations

<u>Pulsating current</u> results in products different from DC. For example, pulsing increases the ratio of <u>ozone</u> to oxygen produced at the anode in the electrolysis of an aqueous acidic solution such as dilute sulphuric acid.^[22] Electrolysis of ethanol with pulsed current evolves an aldehyde instead of primarily an acid.^[23]

Related processes

<u>Galvanic cells</u> and <u>batteries</u> use spontaneous, energy-releasing <u>redox reactions</u> to generate an electrical potential that provides useful power. When a <u>secondary battery</u> is charged, its redox reaction is run in reverse and the system can be considered as an electrolytic cell.

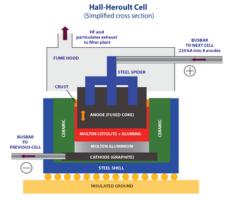
Industrial uses

- Electrometallurgy of aluminium, lithium, sodium, potassium, magnesium, calcium, and in some cases copper.
- Production of chlorine and sodium hydroxide, called the Chloralkali process.
- Production of sodium chlorate and potassium chlorate.

- Production of perfluorinated organic compounds such as trifluoroacetic acid by the process of electrofluorination.
- Purifying copper from refined copper.
- Production of fuels such as <u>hydrogen</u> for <u>spacecraft</u>, <u>nuclear submarines</u> and <u>vehicles</u>.
- <u>Rust removal</u> and cleaning of old coins and other metallic objects.

Manufacturing processes

In manufacturing, electrolysis can be used for:



Hall-Heroult process for producing aluminium

- <u>Electroplating</u>, where a thin film of metal is deposited over a substrate material. Electroplating is used in many industries for either functional or decorative purposes, as in-vehicle bodies and nickel coins.
- <u>Electrochemical machining</u> (ECM), where an electrolytic cathode is used as a shaped tool for removing material by anodic oxidation from a workpiece. ECM is often used as a technique for deburring or for etching metal surfaces like tools or knives with a permanent mark or logo.

Competing half-reactions in solution electrolysis

Using a cell containing inert platinum electrodes, electrolysis of aqueous solutions of some salts leads to the reduction of the cations (such as metal deposition with, for example, zinc salts) and oxidation of the anions (such as the evolution of bromine with bromides). However, with salts of some metals (such as sodium) hydrogen is evolved at the cathode, and for salts containing some anions (such as sulfate SO_4^{2-}) oxygen is evolved at the anode. In both cases, this is due to water being reduced to form hydrogen or oxidized to form oxygen. In principle, the voltage required to electrolyze a salt solution can be derived from the standard electrode potential for the reactions at the anode and cathode. The standard electrode potential is directly related to the Gibbs free energy, ΔG , for the reactions at each electrode and refers to an electrode with no current flowing. An extract from the table of standard electrode potential is shown below.

Half-reaction	<i>E</i> ° (V)	Ref.
$\underline{Na}^+ + e^- \rightleftharpoons Na(\underline{s})$	-2.71	[24]
$\underline{Zn}^{2+} + 2 e^{-} \Rightarrow Zn(\underline{s})$	-0.7618	[25]
2 H ⁺ + 2 e [−] ≓ H ₂ (g)	≡ 0	[25]
Br ₂ (aq) + 2 e [−] ≓ 2 Br [−]	+1.0873	[25]
$O_2(g) + 4 H^+ + 4 e^- = 2 H_2O$	+1.23	[24]
$Cl_2(g) + 2 e^- \Rightarrow 2 Cl^-$	+1.36	[24]
$S_2O_8^{2^-} + 2 e^- \Rightarrow 2 SO_4^{2^-}$	+2.07	[24]

In terms of electrolysis, this table should be interpreted as follows:

- Moving *down* the table, *E*° becomes more positive, and species on the *left* are more likely to be *reduced*: for example, zinc ions are more likely to be reduced to zinc metal than sodium ions are to be reduced to sodium metal.
- Moving up the table, E° becomes more negative, and species on the right are more likely to be oxidized: for example, sodium metal is more likely to be oxidized to sodium ions than zinc metal is to be oxidized to zinc ions.

Using the <u>Nernst equation</u> the <u>electrode potential</u> can be calculated for a specific concentration of ions, temperature and the number of electrons involved. For pure water (pH 7):

- the electrode potential for the reduction producing hydrogen is -0.41 V,
- the electrode potential for the oxidation producing oxygen is +0.82 V.

Comparable figures calculated in a similar way, for 1 M <u>zinc bromide</u>, $ZnBr_2$, are -0.76 V for the reduction to Zn metal and +1.10 V for the oxidation producing bromine. The conclusion from these figures is that hydrogen should be produced at the cathode and oxygen at the anode from the electrolysis of water—which is at variance with the experimental observation that zinc metal is deposited and bromine is produced.^[26] The explanation is that these calculated potentials only indicate the thermodynamically preferred reaction. In practice, many other factors have to be taken into account such as the kinetics of some of the reduction and oxidation of water than predicted, and these are termed <u>overpotentials</u>. Experimentally it is known that overpotentials depend on the design of the cell and the nature of the electrodes.

For the electrolysis of a neutral (pH 7) sodium chloride solution, the reduction of sodium ion is thermodynamically very difficult and water is reduced evolving hydrogen leaving hydroxide ions in solution. At the anode the oxidation of chlorine is observed rather than the oxidation of water since the overpotential for the oxidation of <u>chloride</u> to <u>chlorine</u> is lower than the overpotential for the oxidation of <u>chloride</u> ions and dissolved chlorine gas react further to form <u>hypochlorous acid</u>. The aqueous solutions resulting from this process is called <u>electrolyzed water</u> and is used as a disinfectant and cleaning agent.

Research trends

Electrolysis of carbon dioxide

The electrochemical reduction or electrocatalytic conversion of \underline{CO}_2 can produce value-added chemicals such <u>methane</u>, <u>ethylene</u>, <u>ethanol</u>, etc.^{[27][28][29]} The electrolysis of carbon dioxide gives formate or carbon monoxide, but sometimes more elaborate organic compounds such as ethylene.^[30] This technology is under research as a carbon-neutral route to organic compounds. ^{[31][32]}

Electrolysis of acidified water

Electrolysis of water produces hydrogen and oxygen in a ratio of 2 to 1 respectively.

$$2 H_2O(I) \rightarrow 2 H_2(g) + O_2(g)$$
 $E^\circ = +1.229 V$

The <u>energy efficiency</u> of water electrolysis varies widely. The efficiency of an electrolyzer is a measure of the enthalpy contained in the hydrogen (to undergo combustion with oxygen or some other later reaction), compared with the input electrical energy. Heat/enthalpy values for hydrogen are well published in science and engineering texts, as 144 MJ/kg. Note that fuel cells (not electrolyzers) cannot use this full amount of heat/enthalpy, which has led to some confusion when calculating efficiency values for both types of technology. In the reaction, some energy is lost as heat. Some reports quote efficiencies between 50% and 70% for alkaline electrolyzers; however, much higher practical efficiencies are available with the use of polymer electrolyte membrane electrolysis and catalytic technology, such as 95% efficiency.^{[33][34]}

The <u>National Renewable Energy Laboratory</u> estimated in 2006 that 1 kg of hydrogen (roughly equivalent to 3 kg, or 4 liters, of petroleum in energy terms) could be produced by wind powered electrolysis for between US\$5.55 in the near term and US\$2.27 in the longer term.^[35]

About 4% of hydrogen gas produced worldwide is generated by electrolysis, and normally used onsite. Hydrogen is used for the creation of ammonia for fertilizer via the <u>Haber process</u>, and converting heavy petroleum sources to lighter fractions via <u>hydrocracking</u>. Recently, onsite electrolysis has been utilized to capture hydrogen for hydrogen fuel-cells in <u>hydrogen vehicles</u>.

Carbon/hydrocarbon assisted water electrolysis

Recently, to reduce the energy input, the utilization of carbon (coal), <u>alcohols</u> (hydrocarbon solution), and organic solution (glycerol, formic acid, <u>ethylene glycol</u>, etc.) with co-electrolysis of water has been proposed as a viable option.^{[36][37]} The carbon/hydrocarbon assisted water electrolysis (so-called CAWE) process for hydrogen generation would perform this operation in a single <u>electrochemical</u> reactor. This system energy balance can be required only around 40% electric input with 60% coming from the chemical energy of carbon or hydrocarbon.^[38] This process utilizes solid coal/carbon particles or powder as fuels dispersed in acid/alkaline electrolyte in the form of slurry and the carbon contained source co-assist in the electrolysis process as following theoretical overall reactions:^[39]

Carbon/Coal slurry (C +
$$2H_2O$$
) \rightarrow CO₂ + $2H_2$ $E' = 0.21$ V (reversible voltage) / $E' = 0.46$ V (thermo-neutral voltage)

or

Carbon/Coal slurry (C + H₂O) \rightarrow CO + H₂ E' = 0.52 V (reversible voltage) / E' = 0.91 V (thermo-neutral voltage)

Thus, this CAWE approach is that the actual cell overpotential can be significantly reduced to below 1.0 V as compared to 1.5 V for conventional water electrolysis.

Electrocrystallization

A specialized application of electrolysis involves the growth of conductive crystals on one of the

electrodes from oxidized or reduced species that are generated in situ. The technique has been used to obtain single crystals of low-dimensional electrical conductors, such as <u>charge-transfer salts</u> and linear chain compounds^{[40][41]}

See also

- Alkaline water electrolysis
- Castner–Kellner process
- Electrolytic cell
- Electrochemical engineering
- Faraday's law of electrolysis
- Faraday constant
- Faraday efficiency
- Galvanic corrosion
- Galvanoluminescence
- Gas cracker
- Hall–Héroult process
- High-pressure electrolysis
- Overpotential
- Patterson Power Cell
- Thermochemical cycle
- Timeline of hydrogen technologies
- PEM electrolysis

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