**Electrolysis**

In chemistry and manufacturing, **electrolysis** is a technique that uses a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell. The voltage that is needed for electrolysis to occur is called the decomposition potential.

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**History**
The word "electrolysis" was introduced by Michael Faraday in the 19th century, on the suggestion of the Rev. William Whewell, using the Greek words ἤλεκτρον [ɛ̌ːlektron] "amber", which since the 17th century was associated with electric phenomena, and λύσις [lýsis] meaning "dissolution". Nevertheless, electrolysis, as a tool to study chemical reactions and obtain pure elements, precedes the coining of the term and formal description by Faraday.

In the early nineteenth century, William Nicholson and Anthony Carlisle sought to further Volta's experiments. They attached two wires to either side of Volta's battery and placed it 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. [1]

In 1785 a Dutch Scientist named Martinus Van Marum created an electrostatic generator that he used to reduce tin, zinc and antinomy from their Salts using a process later to be known as electrolysis. Though Martinus Van Marum unknowingly produced electrolysis it was not until 1800 when William Nicholson and Anthony Carlisle discovered the process of how electrolysis works.[2]

When it comes to the beginning of the study of electrolysis, the roots come back to Luigi Galvani's experiments in 1791 with frog legs. His thought was that by placing an animal muscle between two dissimilar metal sheets it could produce electricity. Responding to these claims, Alessandro Volta conducted his own tests.[3][4] This would give insight to Humphry Davy's ideas on electrolysis. During the preliminary experiments, Humphry Davy hypothesis combination of two elements together to form a compound is electrical energy. 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.[5]

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 William Thomas Brande 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. [6][7]

During the later years of Humphry Davy's research, Michael Faraday would become his assistant. Thus, while studying the process of electrolysis under Humphry Davy, Michael Faraday discovered two Laws of Electrolysis.[4]

- The first law States: "The mass of a substance produced at an electrode during electrolysis is proportional to the number of moles of electrons (the quantity of electricity) transferred at that electrode."

- The Second Law States: "The amount of electric charge required to discharge one mole of substance at an electrode is equal to the number of elementary charges on that ion."

During the time of Maxwell and Faraday, concerns came about for electropositive and electronegative activities.[10]

In November 1875, Paul Émile Lecoq de Boisbaudran would discover gallium using electrolysis of gallium hydroxide, producing 3.4 mg of gallium. That following December, he would present

On June 26, 1886, Ferdinand Frederick Henri Moissan finally felt comfortable to perform electrolysis on anhydrous hydrogen fluoride to create a gaseous fluorine pure element. Before he could use hydrogen fluoride, Henri Moissan used fluoride salts with electrolysis. Thus on June 28, 1886 he performed his experiment in front of the Academie des Science to show his discovery of the new element fluorine. [12] In the cost of trying to find elemental fluorine through electrolysis of fluoride salts, many chemists perished such as: Pauline Louyet and Jerome Nickels. [13]

Charles Martin Hall was from America and Paul Hérout was from France. [14] In 1886 they both filed for American patents, with Hérout submitting his in May and Hall’s in July. 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. [15] This became known as the Hall-Héroult process which benefited many industries because the price of aluminum had dropped from four dollars to thirty cents price per pound. [16]

Timeline

- 1785 – Martinus van Marum’s electrostatic generator was used to reduce tin, zinc, and antimony from their salts using electrolysis. [17]
- 1800 – William Nicholson and Anthony Carlisle (view 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 publishes his two laws of electrolysis, provides a mathematical explanation for his laws, and introduces terminology such as electrode, electrolyte, anode, cathode, anion, and cation.
- 1875 – Paul Émile Lecoq de Boisbaudran discovered gallium using electrolysis. [18]
- 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 direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, producing chemical reactions at the electrodes and decomposition of the materials.

The main components required to achieve electrolysis are an electrolyte to carry the ions from one electrode to the other, and a direct current which drives the reaction. The electrolyte is a chemical substance (such as an ion-conducting polymer) that contains free ions, and carries electric current in between the electrodes. If the ions are not mobile, as in most solid salts, then electrolysis cannot occur. The direct current (DC) electrical has to be supplied externally. This
provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.

Electrodes of metal, graphite and semiconductor material are widely used. Choice of suitable electrode 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.\[19\] 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 from the external circuit. The desired products of electrolysis are often in a different physical state from the electrolyte and can be removed by some physical processes. For example, in the electrolysis of brine to produce hydrogen and chlorine, the products are gaseous. These gaseous products bubble from the electrolyte and are collected.\[20\]

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

A liquid containing electrolyte is produced by:

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

An electrical potential is applied across a pair of electrodes immersed in the electrolyte.

Each electrode attracts ions that are of the opposite charge. Positively charged ions (cations) move towards the electron-providing (negative) cathode. Negatively charged ions (anions) move towards the electron-extracting (positive) anode.

In this process electrons are either absorbed or released. Neutral atoms gain or lose electrons and become charged ions that then pass into the electrolyte. The formation of uncharged atoms from ions is called discharging. When an ion gains or loses enough electrons to become uncharged (neutral) atoms, the newly formed atoms separate from the electrolyte. Positive metal ions like Cu\(^{2+}\) deposit onto the cathode in a layer. The terms for this are electroplating, electrowinning, and electrolyrefining. When an ion gains or loses electrons without becoming neutral, its electronic charge is altered in the process. In chemistry, the loss of electrons is called oxidation, while electron gain is called reduction.

** Decomposition potential **

Decomposition potential or decomposition voltage refers to the minimum voltage (difference
in electrode potential) between anode and cathode 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 Nernst equation. Often the actual voltage needed for electrolysis exceeds the thermodynamical value. The additional voltage is referred to as overpotential and is especially high in electrolysis reactions that involve gases, such as oxygen, hydrogen or chlorine. Increasing voltage above the decomposition potential can increase the rate of reaction.

**Oxidation and reduction at the electrodes**

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

\[
Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-
\]

Reduction of ions or neutral molecules occurs at the cathode.

It is possible to reduce ferricyanide ions to ferrocyanide ions at the cathode:

\[
Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}
\]

Neutral molecules can also react at either of the electrodes. For example: p-Benzoquinone can be reduced to hydroquinone at the cathode:

\[
+C_6\text{H}_4\text{O}_2^- + 2 e^- + 2 H^+ \rightarrow C_6\text{H}_4\text{OH} + 2 H_2O
\]

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. Such as when using a Gas diffusion electrode.

**Energy changes during electrolysis**

The amount of electrical energy that must be added equals the change in Gibbs free energy of the reaction plus the losses in the system. The losses can (in theory) be arbitrarily close to zero, so the maximum thermodynamic efficiency equals the enthalpy 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 steam 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 heating value of the produced hydrogen is higher than the electric input.

Variations

Pulsating current results in products different from DC. For example, pulsing increases the ratio of ozone 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 techniques

The following techniques are related to electrolysis:

- Electrochemical cells, including the hydrogen fuel cell, use differences in Standard electrode potential to generate an electrical potential that provides useful power. Though related via the interaction of ions and electrolysis and the operation of electrochemical cells are quite distinct. However, a chemical cell should not be seen as performing electrolysis in reverse.

Faraday's laws of electrolysis

First law of electrolysis

In 1832, Michael Faraday reported that the quantity of elements separated by passing an electric current through a molten or dissolved salt is proportional to the quantity of electric charge passed through the circuit. This became the basis of the first law of electrolysis. The mass of the substance (m) deposited or liberated at an electrode is directly proportional to the quantity of electricity or charge (Q) passed.[24] In this equation k is equal to the electromechanical constant.

\[ m = k \cdot q \]

or

\[ m = e \cdot Q \]

where; e is known as the electrochemical equivalent of the metal deposited or of the gas liberated at the electrode.

Second law of electrolysis

Faraday discovered that when the same amount of current is passed through different
electrolytes/elements connected in series, the mass of substance liberated/deposited at the electrodes is directly proportional to their equivalent weight.

**Industrial uses**

- Electrometallurgy is the process of reduction of metals from metallic compounds to obtain the pure form of metal using electrolysis. Aluminium, lithium, sodium, potassium, magnesium, calcium, and in some cases copper, are produced in this way.
- 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
- Production of electrolytic copper as a cathode, from refined copper of lower purity as an anode.

Electrolysis has many other uses:

- Production of oxygen for spacecraft and nuclear submarines.
- Production of hydrogen for fuel, using a cheap source of electrical energy.

Electrolysis is also used in the cleaning and preservation of old artifacts. Because the process separates the non-metallic particles from the metallic ones, it is very useful for cleaning a wide variety of metallic objects, from old coins to even larger objects including rusted cast iron cylinder blocks and heads when rebuilding automobile engines. Rust removal from small iron or steel objects by electrolysis can be done in a home workshop using simple materials such as a plastic bucket, tap water, lengths of rebar, washing soda, baling wire, and a battery charger.\[25\]

**Manufacturing processes**

In manufacturing, electrolysis can be used for:

- Electroplating, 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.
- Electrochemical machining (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 (e.g., metal deposition with, e.g., zinc salts) and oxidation of the anions (e.g. evolution of bromine with bromides). However, with salts of some metals (e.g. sodium) hydrogen is evolved at the cathode, and for salts containing some anions (e.g. sulfate $\text{SO}_4^{2-}$) 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, $\Delta G$, for the reactions at each electrode and refers to an electrode with no current flowing. An extract from the table of standard electrode potentials is shown below.

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^\circ$ (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}^+ + e^- \rightleftharpoons \text{Na(s)}$</td>
<td>−2.71</td>
<td>[26]</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn(s)}$</td>
<td>−0.7618</td>
<td>[27]</td>
</tr>
<tr>
<td>$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g)$</td>
<td>$\equiv 0$</td>
<td>[27]</td>
</tr>
<tr>
<td>$\text{Br}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Br}^-$</td>
<td>+1.0873</td>
<td>[27]</td>
</tr>
<tr>
<td>$\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$</td>
<td>+1.23</td>
<td>[26]</td>
</tr>
<tr>
<td>$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-$</td>
<td>+1.36</td>
<td>[26]</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}$</td>
<td>+2.07</td>
<td>[26]</td>
</tr>
</tbody>
</table>

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

- Oxidized species (often a cation) with a more negative cell potential are more difficult to reduce than oxidized species with a more positive cell potential. For example, it is more difficult to reduce a sodium ion to a sodium metal than it is to reduce a zinc ion to a zinc metal.
- Reduced species (often an anion) with a more positive cell potential are more difficult to oxidize than reduced species with a more negative cell potential. For example, it is more difficult to oxidize sulfate anions than it is to oxidize bromide anions.

Using the Nernst equation the electrode potential 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 1M zinc bromide, $\text{ZnBr}_2$, 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.[28] 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 reaction steps involved. These factors together mean that a higher potential is required for the reduction and oxidation of water than predicted, and these are termed overpotentials. Experimentally it is

https://en.wikipedia.org/wiki/Electrolysis
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 chlorine to chloride is lower than the overpotential for the oxidation of water to oxygen. The hydroxide ions and dissolved chlorine gas react further to form hypochlorous acid. The aqueous solutions resulting from this process is called electrolyzed water and is used as a disinfectant and cleaning agent.

**Research trends**

**Electrolysis of carbon dioxide**

The electrochemical reduction or electrocatalytic conversion of CO₂ can produce value-added chemicals such methane, ethylene, ethane, etc.[29][30][31] The electrolysis of carbon dioxide gives formate or carbon monoxide, but sometimes more elaborate organic compounds such as ethylene.[32] This technology is under research as a carbon-neutral route to organic compounds.[33][34]

**Electrolysis of acidified water**

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

\[
2 \text{H}_2\text{O(l)} \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}); \quad E_0 = +1.229 \text{ V}
\]

The energy efficiency 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.[35][36]

The National Renewable Energy Laboratory estimated that 1 kg of hydrogen (roughly equivalent to 3 kg, or 4 L, of petroleum in energy terms) could be produced by wind powered electrolysis for between $5.55 in the near term and $2.27 in the long term.[37]

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 Haber process, and converting heavy petroleum sources to lighter fractions via hydrocracking. Recently, onsite electrolysis has been utilised to capture hydrogen for hydrogen fuel-cells in hydrogen vehicles.

https://en.wikipedia.org/wiki/Electrolysis
Carbon/hydrocarbon assisted water electrolysis

Recently, to reduce the energy input, the utilization of carbon (coal), alcohols (hydrocarbon solution), and organic solution (glycerol, formic acid, ethylene glycol, etc.) with co-electrolysis of water has been proposed as a viable option.[38][39] The carbon/hydrocarbon assisted water electrolysis (so-called CAWE) process for hydrogen generation would perform this operation in a single electrochemical reactor. This system energy balance can be required only around 40% electric input with 60% coming from the chemical energy of carbon or hydrocarbon.[40] 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:[41]

Carbon/Coal slurry (C + 2H_2O) -> CO_2 + 2H_2 E' = 0.21 V (reversible voltage) / E' = 0.46 V (thermo-neutral voltage)

or

Carbon/Coal slurry (C + H_2O) -> CO + H_2 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 V as compared to 1.5 V for conventional water electrolys.

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 charge-transfer salts and linear chain compounds[42][43]

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

https://en.wikipedia.org/wiki/Electrolysis
- Patterson Power Cell
- Thermochemical cycle
- Timeline of hydrogen technologies
- PEM electrolysis

References


17. The Supplement (1803 edition) to Encyclopædia Britannica 3rd edition (1797), volume 1, page 225, "Mister Van Marum, by means of his great electrical machine, decomposed the calces of tin, zinc, and antimony, and resolved them into their respective metals and oxygen" and gives as a reference Journal de Physiques, 1785.


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