INDUSTRIAL PROCESS

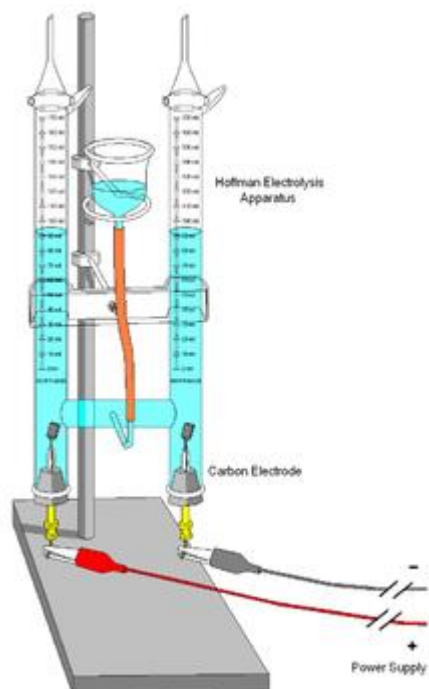**SESSION 4 Electrolysis**

Session 4

Electrolysis

Illustration of an electrolysis apparatus used in a school laboratory.

In chemistry and manufacturing, **electrolysis** is a method of using a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially highly 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.

Contents

History

The word electrolysis comes from the Greek ἤλεκτρον [ĕ:lektron] "amber" and λύσις [lýsis] "dissolution".

- 1785 – Martinus van Marum's electrostatic generator was used to reduce tin, zinc, and antimony from their salts using electrolysis.[1]
- 1800 – William Nicholson and Anthony Carlisle (view also Johann Ritter), decomposed water into hydrogen and oxygen.
- 1807 – Potassium, sodium, barium, calcium and magnesium were discovered by Sir Humphry Davy using electrolysis.
- 1833 - Michael Faraday develops his two laws of electrolysis, and provides a mathematical explanation of his laws.
- 1875 – Paul Émile Lecoq de Boisbaudran discovered gallium using electrolysis.[2]
- 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 passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials.

The main components required to achieve electrolysis are :

- An electrolyte : a substance containing free ions which are the carriers of electric current in the electrolyte. If the ions are not mobile, as in a solid salt then electrolysis cannot occur.
- A direct current (DC) supply : provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.
- Two electrodes : an electrical conductor which provides the physical interface between the electrical circuit providing the energy and the electrolyte

Electrodes of <u>metal</u>, <u>graphite</u> and <u>semiconductor</u> material are widely used. Choice of suitable electrode depends on chemical reactivity between the electrode and electrolyte and the cost of manufacture.

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 <u>brine</u> to produce hydrogen and chlorine, the products are gaseous. These gaseous products bubble from the electrolyte and are collected.[3]

$$2 \ NaCl + 2 \ H_2O \rightarrow 2 \ NaOH + H_2 + Cl_2$$
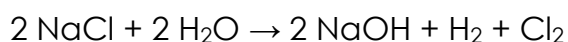
A liquid containing mobile ions (electrolyte) is produced by:

- <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 is melted (*fused*) by heating

An electrical potential is applied across a pair of <u>electrodes</u> immersed in the electrolyte.

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 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^{++} deposit onto the cathode in a layer. The terms for this are <u>electroplating electrowinning</u> and <u>electrorefining</u>. 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.
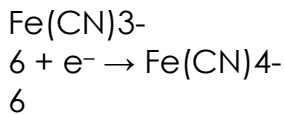
Oxidation and reduction at the electrodes

<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:
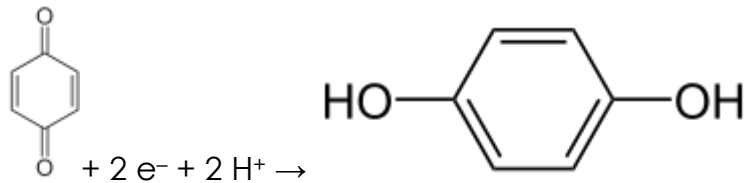
Fe2+
aq → Fe3+
aq + e⁻
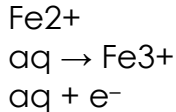
Reduction of ions or neutral molecules occurs at the cathode.

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

Fe(CN)3-
6 + e⁻ → Fe(CN)4-
6

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⁺ →

In the last example, H⁺ ions (hydrogen ions) also take part in the reaction, and are provided by an 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.

Related techniques

The following techniques are related to electrolysis:

- Electrochemical cells, including the hydrogen fuel cell, utilize differences in Standard electrode potential in order to generate an electrical potential from which useful power can be extracted. Although related via the interaction of ions and electrodes, electrolysis and the operation of electrochemical cells are quite distinct. A chemical cell should *not* be thought of as performing "electrolysis in reverse".

Faraday's laws of electrolysis

Main article: 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:

$$m = k \cdot q$$

Second law of electrolysis[

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

Industrial uses[
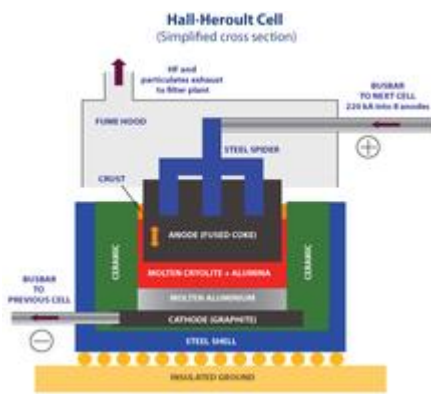
Hall-Heroult process for producing aluminium

- Production of <u>aluminium</u>, <u>lithium</u>, <u>sodium</u>, <u>potassium</u>, <u>magnesium</u>, <u>calcium</u>
- <u>Coulometric</u> techniques can be used to determine the amount of matter transformed during electrolysis by measuring the amount of electricity required to perform the electrolysis
- Production of <u>chlorine</u> and <u>sodium hydroxide</u>
- Production of <u>sodium chlorate</u> and <u>potassium chlorate</u>
- Production of perfluorinated organic compounds such as <u>trifluoroacetic acid</u>
- Production of <u>electrolytic copper</u> as a <u>cathode</u>, from refined <u>copper</u> of lower purity as an <u>anode</u>.

Electrolysis has many other uses:

- <u>Electrometallurgy</u> is the process of reduction of metals from metallic compounds to obtain the pure form of metal using electrolysis. For example, sodium hydroxide in its molten form is separated by electrolysis into sodium and oxygen, both of which have important chemical uses. (Water is produced at the same time.)
- <u>Anodization</u> is an electrolytic process that makes the surface of metals resistant to <u>corrosion</u>. For example, ships are saved from being corroded by oxygen in the water by this process. The process is also used to decorate surfaces.
- Production of <u>oxygen</u> for <u>spacecraft</u> and <u>nuclear submarines</u>.
- <u>Electroplating</u> is used in layering metals to fortify them. Electroplating is used in many industries for functional or decorative purposes, as in vehicle bodies and nickel coins.
- Production of hydrogen for fuel, using a cheap source of electrical energy.
- Electrolytic Etching of metal surfaces like tools or knives with a permanent mark or logo.

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 <u>rusted</u> <u>cast iron</u> <u>cylinder blocks</u> and <u>heads</u> when rebuilding automobile engines.

Competing half-reactions in solution electrolysis[

Using a cell containing inert platinum electrodes, electrolysis of aqueous solutions of some salts leads to 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 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 potentials is shown below.

Half-reaction	$E°$ (V)	Ref.
$Na^+ + e^- \rightleftharpoons Na(s)$	−2.71	[4]
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.7618	[5]
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**≡ 0**	[5]
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.0873	[5]
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23	[4]
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.36	[4]
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.07	[4]

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, $ZnBr_2$, 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.[6] 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 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 chloride to chlorine 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.

Electrolysis of water

Main article: Electrolysis of water

One important use of electrolysis of water is to produce hydrogen.

$$2 H_2O(l) \rightarrow 2 H_2(g) + O_2(g); E_0 = -1.229 \text{ V}$$
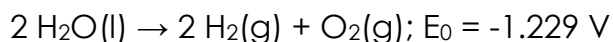
Hydrogen can be used as a fuel for powering internal combustion engines by combustion or electric motors via hydrogen fuel cells (see *Hydrogen vehicle*). This has been suggested as one approach to shift economies of the world from the current state of almost complete dependence upon hydrocarbons for energy (See *hydrogen economy*.) There are a wide range of conventional and emerging technologies being explored for the production of hydrogen from

water including low temperature electrolysis, high temperature electrolysis and chemically assisted electrolysis[7][8]

The underline energy efficiency of water electrolysis varies widely. The efficiency of an electrolyser is a measure of the enthalpy contained in the hydrogen (to under go 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 electrolysers) cannot utilise 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 electrolysers; however, much higher practical efficiencies are available with the use of PEM (Polymer Electrolyte Membrane electrolysis) and catalytic technology, such as 95% efficiency.[9][10] In the US there is still an occasional erroneous tendency to use the 'Lower Heating Value' for efficiencies. This value (becoming obsolete) does not represent the total amount of energy within the hydrogen, hence the efficiency appears lower than when using the more accurately defined values. The theoretical maximum considers the total amount of energy required for the formation of the hydrogen and oxygen from water. Note that (in more broader contexts of energy efficiency), these values refer only to the efficiency of converting electrical energy into hydrogen's chemical energy; the energy lost in generating the electricity is not included.

NREL 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.[11]

About 4% of hydrogen gas produced worldwide is created 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.

Electro crystallization

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.

Experimenters

Scientific pioneers of electrolysis include:

- Antoine Lavoisier
- Robert Bunsen
- Humphry Davy
- Michael Faraday
- Paul Héroult
- Svante Arrhenius
- Adolph Wilhelm Hermann Kolbe
- William Nicholson
- Joseph Louis Gay-Lussac
- Alexander von Humboldt
- Johann Wilhelm Hittorf
- Kai Grjotheim

Pioneers of batteries:

- Alessandro Volta
- Gaston Planté

More recently, electrolysis of heavy water was performed by Fleischmann and Pons in their famous experiment, resulting in anomalous heat generation and the discredited claim of cold fusion

electrolysis of brine: what forms at the anode?

chlorine gas

☐☐☐

electrolysis of brine: what forms at the cathode?

hydrogen gas

☐☐☐

electrolysis of brine: what is left in solution?

sodium hydroxide (NaOH)

☐☐☐

electrolysis of brine: what can pass through the membrane?

positive ions (Na+)

☐☐☐

electrolysis of brine: how do we test for the product formed at the anode?
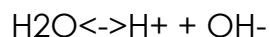
damp blue litmus paper- bleached

☐☐☐

electrolysis of brine: where does the hydrogen come from?

dissociation of water

☐☐☐

equation for ionisation of water

$H_2O <-> H^+ + OH^-$

☐☐☐

uses of sodium hydroxide, NaOH

Bleach, soap, paper

☐☐☐

uses of chlorine

sterilising water, bleach, hydrochloric acid

☐☐☐

products of electrolysis of sulfuric acid H2SO4

anode- oxygen, cathode- hydrogen

☐☐☐

products of electrolysis of copper sulfate CuSO4

anode- oxygen, cathode- copper

☐☐☐

electrolysis of brine: what separates the products?

diaphragm cell