

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:

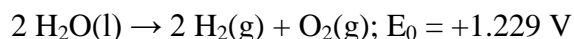
$$m = k \cdot q$$

Second law of electrolysis

Faraday also discovered that the mass of the resulting separated elements is directly proportional to the atomic masses of the elements when an appropriate integral divisor is applied. This provided strong evidence that discrete particles of matter exist as parts of the atoms of elements.

Electrolysis of water

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



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*.)

The energy efficiency of water electrolysis varies widely. The efficiency is a measure of what fraction of electrical energy used is actually contained within the hydrogen. Some of the electrical energy is converted to heat, an almost useless byproduct.

Some reports quote efficiencies between 50% and 70%. This efficiency is based on the Lower Heating Value of Hydrogen. The Lower Heating Value of Hydrogen is total thermal energy released when hydrogen is combusted minus the latent heat of vaporisation of the water. This does not represent the total amount of energy within the hydrogen, hence the efficiency is lower than a more strict definition. Other reports quote the theoretical maximum efficiency of electrolysis as being between 80% and 94%. The theoretical maximum considers the total amount of energy absorbed by both the hydrogen and oxygen. 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. For instance, when considering a power plant that converts the heat of nuclear reactions into hydrogen via electrolysis, the total efficiency is more likely to be between 25% and 40%.

NREL found that a kilogram of hydrogen (roughly equivalent to a gallon of gasoline) could be produced by wind powered electrolysis for between \$5.55 in the near term and \$2.27 in the long term.

About four percent 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 hydro cracking.

Electro-Refining Operations

Copper anodes from the converter process are dissolved electrolytically using an acid copper sulphate solution as an electrolyte. The products of this operation are pure copper cathodes and an anode slime which may contain gold and small quantities of the platinum group metals. The cells are constructed of rubber-lined concrete. Internal measurements are approximately 84 x 2 x 3 feet. The warmed electrolyte is fed in at one end and overflows from the other into a launder running between the lines of cells. From the launder the liquid is pumped to overhead tanks where its heat is maintained, and by gravity flows to a manifold which feeds it back to the cells. During electrolysis the electrolyte tends to accumulate nickel and quantities have to be bled off occasionally and replaced by pure copper sulphate.

The impure electrolyte is treated for recovery of the copper sulphate and the nickel sulphate is passed to the nickel refinery. There are **21** anodes and 20 cathodes in each cell and a current of 15; amp per square foot is maintained. The quantity of anode slime formed by the dissolving of these anodes is small and falls to the bottom of the cells, where it is periodically recovered. The dissolving of the nickel anodes follows the same general pattern, the products being pure nickel cathodes and an anode slime containing the bulk of the platinum group metals. In this case the electrolyte is a neutral solution of nickel sulphate containing boric acid as a buffer and has to be continually purified to produce a pure cathode.

Copper and iron are present in the anodes and being more electro-negative than nickel must be removed from the electrolyte or they will deposit on the cathode as impurities. To achieve this each cathode is placed in a calico bag with purified electrolyte flowing into it, so that the cathode will grow in clean liquor. The stripped liquor flows out of the bag laterally and picks up the impurities from the solution of the anode. This liquor flows out of each cell into a launder and is pumped across to large circular treatment tanks where it is heated to approximately 70°C. An emulsion of nickel carbonate is added to adjust the pH and *air* is blown through to hydrolyse out the iron. After this any copper present is precipitated and the contents pumped through a filter press to separate out the solid impurities.

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