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 required products of electrolysis are in some 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.

$$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + H_2 + Cl_2$$

A liquid containing mobile ions (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 (*fused*) 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, whereas negatively charged ions (anions) move towards the positive anode.

At the electrodes, electrons are absorbed or released by the atoms and ions. Those atoms that gain or lose electrons to become charged ions pass into the electrolyte. Those ions that gain or lose electrons to become uncharged atoms separate from the electrolyte. The formation of uncharged atoms from ions is called discharging.

The energy required to cause the ions to migrate to the electrodes, and the energy to cause the change in ionic state, is provided by the external source of electrical potential.

Oxidation and reduction at the electrodes

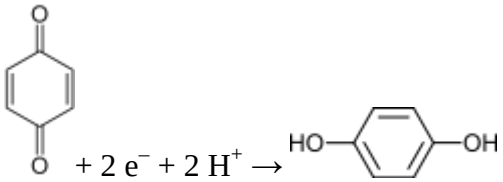
Oxidation of ions or neutral molecules occurs at the anode, and the reduction of ions or neutral molecules occurs at the cathode. For example, it is possible to oxidize ferrous ions to ferric ions at the anode:

$$Fe^{2+}_{aq} \rightarrow Fe^{3+}_{aq} + e^-$$

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

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

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



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

The substances oxidised or reduced can also be the solvent (usually water) or the electrodes. It is possible to have electrolysis involving gases.

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. Heat is absorbed from the surroundings, and the heating value of the produced hydrogen is higher than the electric input.

Source: http://nprcet.org/e%20content/Misc/e-Learning/EEE/IV%20YEAR/EE1452%20-%20Electric%20Energy%20Generation,%20Conservation%20and%20Utilization.pdf