

# Electrolysis

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The use of electric current to stimulate a non-spontaneous reaction. Electrolysis can be used to separate a substance into its original components/elements and it was through this process that a number of elements have been discovered and are still produced in today's industry. In Electrolysis, an electric current is sent through an electrolyte and into solution in order to stimulate the flow of ions necessary to run an otherwise non-spontaneous reaction. Processes involving electrolysis include: *electro-refining*, *electro-synthesis*, and the *chloro-alkali* process.

## Electrolytic Cell vs Voltaic Cell

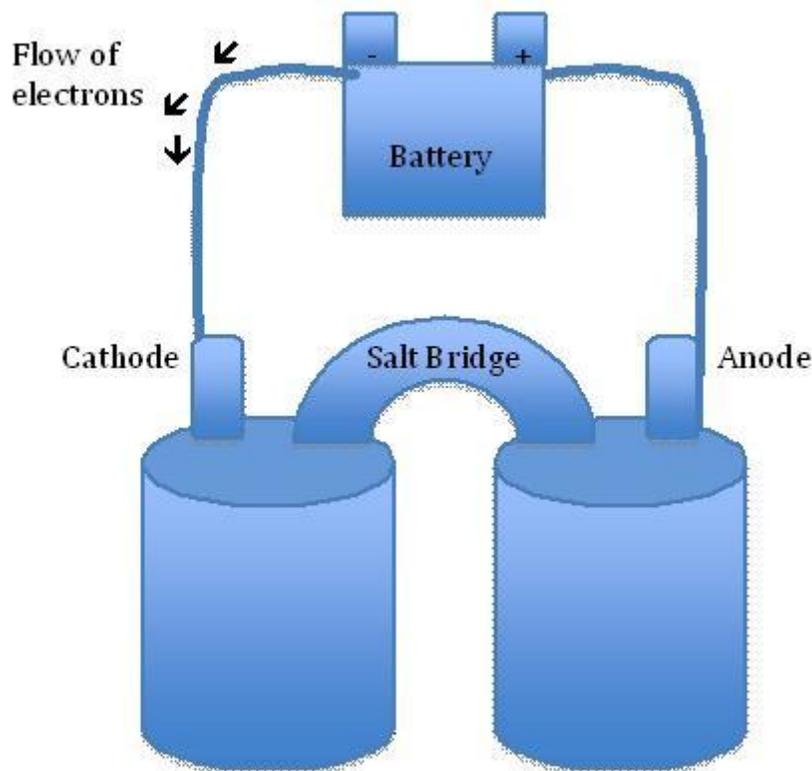
Example: When we electrolyze water by passing an electric current through it, we can separate it into hydrogen and oxygen.



More information : The Electrolysis of Water

An electrolytic cell is essentially the non-spontaneous reaction's voltaic cell, (in fact if we reversed the flow of electricity within a voltaic cell by exceeding a required voltage, we would create an electrolytic cell). Electrolytic cells consist of two electrodes (one that acts as a cathode and one that acts as an anode), and an electrolyte. Unlike a voltaic cell, reactions using electrolytic cells must be electrically induced and its anode and cathode are reversed (anode on the left, cathode on the right).

Voltaic	Electrolytic
Oxidation: $\text{X} \rightarrow \text{X}^+ + \text{e}^-$ (Negative Anode)	$\text{Y} \rightarrow \text{Y}^+ + \text{e}^-$ (Positive Anode)
Reduction: $\text{Y}^+ + \text{e}^- \rightarrow \text{Y}$ (Positive Cathode)	$\text{X}^+ + \text{e}^- \rightarrow \text{X}$ (Negative Cathode)
Overall: $\text{X} + \text{Y}^+ \rightarrow \text{X}^+ + \text{Y}$ ( $G < 0$ )	$\text{X}^+ + \text{Y} \rightarrow \text{X} + \text{Y}^+$ ( $G > 0$ )
This reaction is <b>spontaneous</b> and will release energy	This reaction is <b>non-spontaneous</b> and will absorb energy



## Factors Affecting Electrolysis Reactions

1. Overpotential- The generated voltage is significantly higher than expected. An overpotential may be necessary to overcome interactions taking place on the electrode itself (especially for gasses).
2. Electrode type- An inert electrode acts as a surface for a reaction to occur on and is not involved in the chemical reaction whereas an active electrode becomes a part of the half reaction.
3. Simultaneous electrode reactions- If two different pairs of half-reactions take place at once. Some half reactions should be eliminated in order to determine a single pair of half reactions best suited for the electrolysis to occur.
4. The state of reactants- If reactants are in nonstandard states, the voltage of half cells may differ from that of the standard amount. In this case, the solution for the anode half cell may have a pH that is either higher or lower than the standard pH of 4 which may lead to a nonstandard voltage as well.

## Calculations

*Faraday's Constant*-The amount of electric charge associated with one mole of electrons.

Faraday's Constant: 1 mole  $e^-$  = 96,485 C (where C measures Coulombs)

To find the amount of moles of electrons that have been involved in an electrolysis reaction use the following equation:

$$\text{Charge (C)} = \text{current (C/s)} \times \text{time (s)} \times (1 \text{ mole } e^- / 96,485 \text{ C})$$

## Application

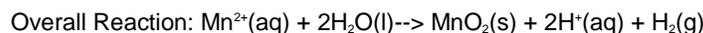
Several processes of electrolysis are used in today's industry:

### 1. **Electrorefining**

the anode is the impure metal and any impurities are removed during the process of electrolysis when the metal travels from anode to cathode. During the electrorefining of metals, the cathode has a decomposition of pure metals from a solution containing the metal ion. For example copper is purified through electrolysis in order to be used for applications that require high electrical conductivity. During this process, the cathode is a pure piece of copper, while the anode is an impure piece of copper. The  $\text{Cu}^{2+}$  from the anode moves through a sulfuric acid-copper(II) sulfate solution into the cathode where it becomes solid copper. While this is occurring, the impurities are left at the bottom of the tank. This leftover residue is called anode mud. The electrolysis is carried out at 0.15 - 0.30V (low voltage) in order to make sure that Ag, Au, and Pt impurities are not oxidized while in the anode and become anode mud. Whereas most of the other components become oxides or hydroxides and form water-soluble species.

### 2. **Electrosynthesis**

a method which uses electrolysis reactions to produce certain products. For example  $\text{MnO}_2$  needs to undergo electrolysis in order to be used for alkaline batteries. The solution for the electrosynthesis of  $\text{MnO}_2$  is  $\text{MnSO}_4$  in  $\text{H}_2\text{SO}_4$ . The anode is graphite, where  $\text{Mn}^{2+}$  is oxidized. While at the cathode, hydrogen is reduced from  $\text{H}^+$  to  $\text{H}_2$ .



### 3. **Chloro-Alkali Process**

Electrolysis of seawater which leads to the production of chlorine and the alkali, sodium hydroxide. There are 3 different methods in which these two components are produced: membrane cell, diaphragm cell, and mercury cell process.

### 3. **Mercury Cell Process**

Electrolysis of seawater in a mercury cell leads to the production of chlorine and sodium hydroxide at the same time. This method involves using mercury as the cathode and graphite as the anode. The mercury attracts either sodium or potassium cations and the mercury forms an amalgam with it. However when the amalgam is introduced to water it forms sodium hydroxide and hydrogen leaving the mercury to be reused later. The chlorine gas is left to form at the anode.

### 4. **Diaphragm Cell Process**

The diaphragm cell has  $\text{Cl}_2$  being released from the anode section, while there is  $\text{H}_2$  being released from the cathode section. If  $\text{Cl}_2$  manages to mix with  $\text{NaOH}$ , the  $\text{Cl}$  turns into other products. Therefore the diaphragm cell has a bigger amount of  $\text{NaCl}$ , and a smaller amount of solution in the cathode in order for the  $\text{NaCl}$  to come in contact with the other solution gradually, while simultaneously preventing backflow of  $\text{NaOH}$ .

### 5. **Membrane Cell Process**

This process is more efficient than others as it does not use mercury and does not require a significant amount of energy. Contains a cation-exchange membrane which is usually made from fluorocarbon polymer. This membrane allows hydrated cations to pass in between the anode and cathode compartments, but does not allow the backflow of the ions,  $\text{Cl}^-$  and  $\text{OH}^-$ . This allows the sodium hydroxide produced to have less contamination by chloride ions.

## References

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