

Electrolysis of Water

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Introduction

Passage of an electric current through water causes positive ions, including the inherent hydrogen ions H_3O^+ , to move towards the negative electrode (cathode) and negative ions, including the inherent hydroxide ions OH^- , to move towards the positive electrode (anode). At sufficient potential difference, this may may cause electrolysis with oxygen gas being produced at the anode and hydrogen gas produced at the cathode (see [1878] for current reviews). The electrolysis of water usually involves dilute, or moderately concentrated, salt solutions in order to reduce the power loss driving the current through the solution, but the presence of salt is not a requirement for electrolysis.

Thus,

Anode	+ve	$6\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}_3\text{O}^+(\text{aq}) + 4\text{e}^-(\text{to anode})^{\text{b}}$	$E^{\text{p}} = +1.229 \text{ V},^{\text{a}} \text{ pH } 0$	$E^{\text{p}'} = +0.815 \text{ V}^{\text{a}}$
Cathode	-ve	$4\text{e}^-(\text{from cathode}) + 4\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq})$	$E^{\text{p}} = -0.828 \text{ V}, \text{ pH } 14$	$E^{\text{p}'} = -0.414 \text{ V}$

where (l), (g) and (aq) show the states of the material as being liquid, gas or aqueous solution and with the electrical circuit passing the electrons back from the anode to the cathode. The reactions are heterogeneous, taking place at the boundary between the electrode and the electrolyte with the aqueous boundary layer subject to concentration and electrical potential gradients with the presence of the generated gaseous [nanobubbles](#) and microbubbles.

Generally the water next to the electrodes^f will change pH due to the ions produced or consumed. If the electrode compartments are separated by a suitable porous membrane then the concentration of H_3O^+ in the anolyte and OH^- in the catholyte (and hence the increase in the respective conductivities) are both expected to increase more than if there is free mixing between the electrodes, when most of these ions will neutralise each other. Small but expected differences in the solutions' pHs next to the anode (anolyte) and cathode (catholyte) cause only a slight change to the overall potential difference required (1.229 V). Increasing the acid content next to the anode due to the H_3O^+ produced will increase its electrode potential (for example: pH 5 $E = +0.933 \text{ V}$) and increasing the alkaline content next to the cathode due to the OH^- produced will make its electrode potential more negative (for example: pH 9 $E = -0.532 \text{ V}$).

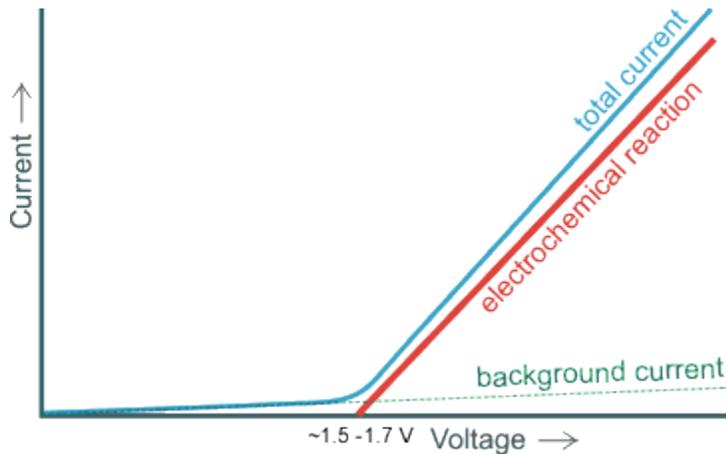
The amount of product formed can be calculated directly from the current flowing, as 96,485 coulombs (*i.e.* one [faraday](#)) delivers one [mole](#) of electrons; with one faraday ideally producing 0.5 moles of H_2 plus 0.25 moles of O_2 . Thus, one amp flowing for one second (one coulomb) produces 5.18 μmol H_2 (10.455 μg , 0.1177 ml at [STD](#)) and 2.59 μmol O_2 (82.888 μg , 0.0588 ml at STD; 4.9 kW h/m³ H_2 at 60% efficiency), if there are no side reactions at the electrodes; that is

$$\text{Number of moles} = \frac{\text{Coulombs}}{(\text{unsigned numeric charge on the ion} \times \text{Faraday})}$$

$$\text{Number of moles} = \frac{(\text{Current in amperes} \times \text{time in seconds})}{(\text{unsigned numeric charge on the ion} \times \text{Faraday})}$$

The gasses produced at the electrodes may dissolve, with their equilibrium solubility proportional to their partial pressure as gasses in the atmosphere above the electrolytic surface. Oxygen gas is poorly soluble ($\sim 44 \text{ mg kg}^{-1}$, $\sim 1.4 \text{ mM}$ at 0.1 MPa and 20 °C, but only $\sim 0.29 \text{ mM}$ against its normal atmospheric partial pressure). Hydrogen gas is less soluble ($\sim 1.6 \text{ mg kg}^{-1}$, $\sim 0.80 \text{ mM}$ at 0.1 MPa and 20 °C but only $\sim 0.44 \text{ nM}$ against its very low normal atmospheric partial pressure).

Although theoretically as above, the current passing should determine the amounts of hydrogen and oxygen formed, several factors ensure that somewhat lower amounts of gas are actually found. Some electrons (and product) are used up in side reactions, some of the products are catalytically reconverted to water at the electrodes particularly if there is no membrane dividing the electrolysis compartments, some hydrogen may absorb into the cathode (particularly if palladium is used) and some oxygen oxidizes the anode. Finally some gas remains held up in the nanobubbles for a considerable time and some gas may escape measurement.

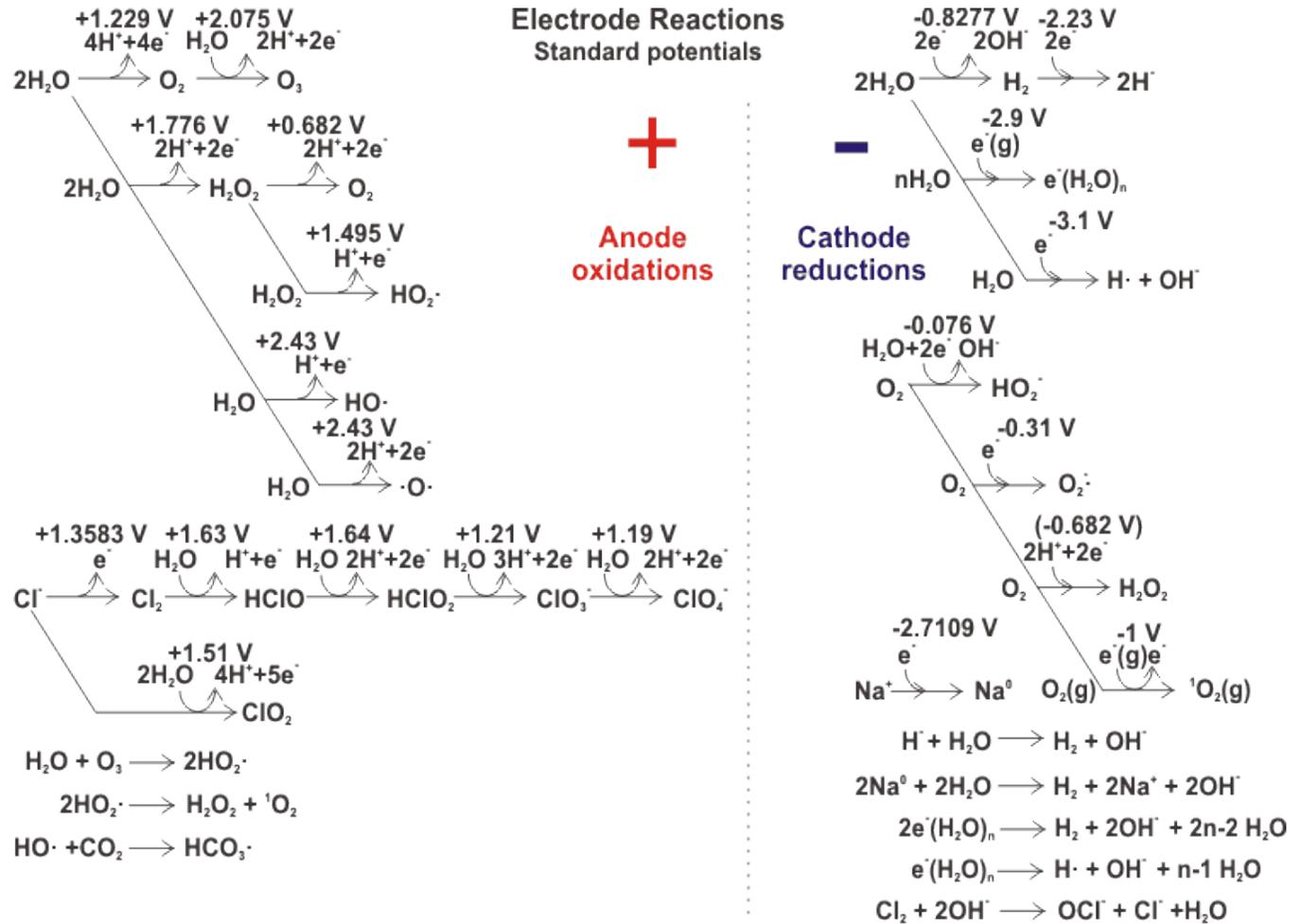


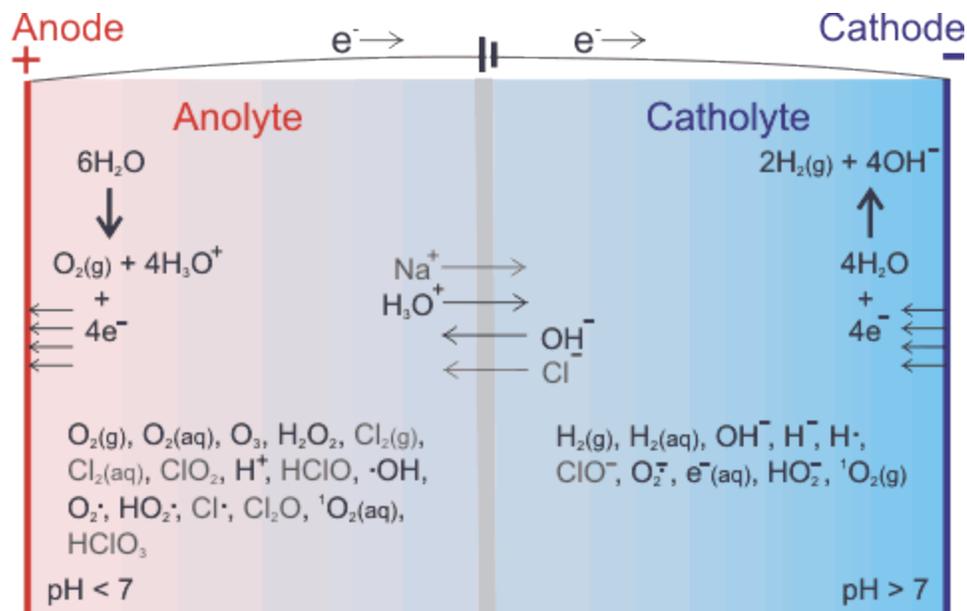
The above description hides much important science and grossly over-simplifies the system. The actual potential required at any position within the electrolytic cell is determined by the localized concentration of the reactants and products including the local pH of the solution, instantaneous gas partial pressure and electrode surface loss due to attached gas bubbles. In addition, a greater potential difference (called overpotential) is required at both electrodes to deliver a significant reaction rate. Typically at good electrodes, such as those made of platinum, that may total an addition of about half a volt to the potential difference between the electrodes. In addition a further potential difference is required to drive the current through the electrical resistance of electrolytic cell and circuit; for a (typical) one ohm cell circuit resistance, each amp current flow would require a further one volt. This power (and consequent energy) loss ($\sim 20\%$, [1978]) causes the electrolyte to warm up during electrolysis.

The efficiency of electrolysis increases with the temperature as the hydrogen bonding reduces [1876]. If the pressure over the electrolysis is increased then more current passes for the same applied voltage. However the output of gas per coulomb and the heating effect are both decreased. This is due to the increased solubility of the gasses and smaller bubbles both reducing the cell resistance and increasing recombination reactions. Although reducing the distance between electrodes reduces the resistance of the electrolysis medium, the process may suffer if the closeness

allows a build up of gas between these electrodes [1876]. Low to higher pulsed potential increases the reaction (current) and accelerates both the movement of bubbles from the electrode surface and the mass transfer rate in the electrolyte, which lowers the electrochemical polarization in the diffusion layer and further increases hydrogen production efficiency [2075]. The rate of change of the current density (and hence efficiency) can be increased using a magnetic field [2075].

Pure water conducts an electric current very poorly and, for this reason, is difficult to electrolyze. However, usually some salts will be added or present in tap and ground waters which will be sufficient to allow electrolysis to proceed at a significant rate. However such salts, and particularly chloride ions, may then undergo redox reactions at an electrode. These side reactions both reduce the efficiency of the electrolysis reactions (above) and produce new solutes. Other electrolytic reactions may occur at the electrodes so producing further solutes and gasses. In addition, these solutes may react together to produce other materials. Together the side reactions are complex and this complexity increases somewhat when the voltage applied to the cell is greater than that required by the above reactions and processes. The likely reactions within the electrode compartments are described below. Some of these may only occur to a very small extent and other reactions may also be occurring that are not included. Standard electrode potentials are shown.



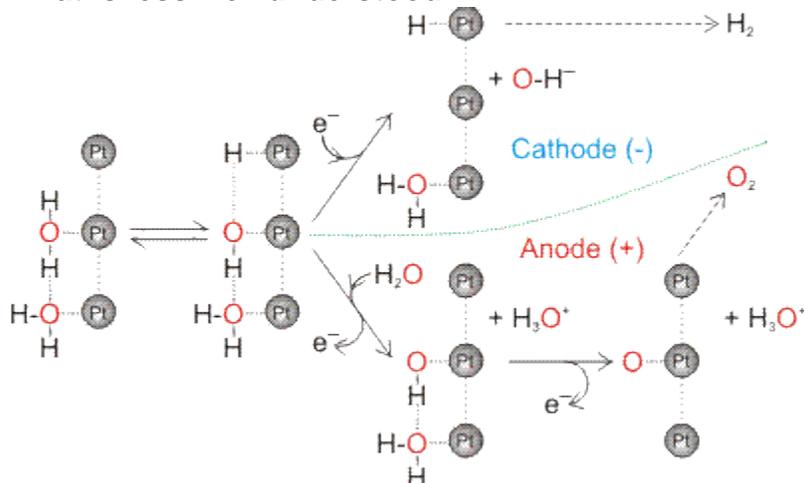


Electrolysis compartments.

Right is given a representation of the compartments in the electrolytic cell with some of their constituent molecules, ions and radicals. Other materials may be present and some of the materials given may be at very low concentrations.

Although charged ions are attracted into the compartments by virtue of the applied potential, oppositely charged ions are created in both compartments due to the electrolytic reactions. Thus for example, Na^+ ions enter the catholyte from the anode compartment but excess OH^- is produced at the same time at the cathode. The concentration of the OH^- ions will be generally expected to be greater than the increase in cations in the catholyte and the concentration of the H_3O^+ ions will be generally expected to be greater than any increase in anions in the anolyte. Often a conductive but semi-permeable membrane (nafion, a sulfonated tetrafluoroethylene based copolymer [1880], for example) is used to separate the two compartments and reduce the movement of the products between the electrode compartments; a process that improves the yield by reducing back and side reactions [1978]. Due to the easier electrolysis of water containing 1H rather than 2H (D) or 3H (T), electrolysis can be used for producing water with reduced or enriched isotopic composition.

What is less well understood?



Although much time has been spent on investigating and modeling the electrolytic system [1877], it is still not entirely clear how water is arranged at the surface of the electrodes. Alignment of the water dipoles with the field is expected, together with the consequential breakage of a proportion of the water molecules' hydrogen bonds. When the electrode processes occur it appears that singly-linked hydrogen atoms and singly-linked oxygen atoms are bound to the platinum atoms at the cathode and anode respectively. These bound atoms are able to diffuse around in two dimensions on the surface of their respective electrodes until they take part in further reaction. Other atoms and polyatomic groups may also bind similarly to the electrode surfaces and subsequently undergo reactions. Molecules such as O₂ and H₂ produced at the surfaces may enter nanoscopic cavities in the liquid water ([nanobubbles](#)) as gasses or become solvated by the water.

Gas-containing cavities in liquid solution (often called bubbles) grow or shrink by diffusion according to whether the solution is over-saturated or under-saturated with the dissolved gas. Given suitable electrodes, the size of the cathodic hydrogen bubbles depends on the overvoltage with nanobubbles being formed at low overvoltages and larger bubbles being formed at higher overvoltages [2068]. Larger micron-plus sized bubbles have sufficient buoyancy to rise through the solution and release contained gas at the surface before all the gas dissolves. With smaller bubbles a pressure is exerted by the surface tension is in inverse proportion to their diameter and they may be expected to collapse. However, as the [nanobubblegas/liquid interface is charged](#), an opposing force to the surface tension is introduced, so slowing or preventing their dissipation. Electrolytic solutions have been proven to contain very large numbers of gaseous nanobubbles [974]. The 'natural' state of such interfaces appears to be negative [1266]. Other ions with low surface charge density (such as Cl⁻, ClO⁻, HO₂⁻ and O₂^{·-}) will also favor the gas/liquid interfaces [928a] as probably do hydrated electrons [1841, 1874]. Aqueous radicals also prefer to reside at such interfaces [939]. From this known information it seems clear that the nanobubbles present in the catholyte will be negatively charged but those in the anolyte [1881] will probably possess little charge (with the produced excess positive H₃O⁺ ions canceling out the natural negative charge). Therefore, catholyte nanobubbles are not likely to lose their charge on mixing with the anolyte stream and are otherwise known to be stable for many minutes [974]. Additionally gas molecules may become charged within the nanobubbles (such as the superoxide radical ion, O₂^{·-}), due to the excess potential on the cathode, increasing the overall charge of the nanobubbles and, probably, the stability of that charge. Raised temperature at the electrode surface, due to the excess power loss over that required for the electrolysis, may also increase nanobubble formation by reducing local gas solubility. Clearly increasing the pressure on solutions containing nanobubbles will also slow down their dissipation if this pressure has increased the dissolved gas content.

Driving cars using water?

The hydrogen produced by electrolysis may be used as a fuel but the overall efficiency of the process is always well below 100%. Thus the hydrogen produced can never be used to drive the electrolysis that produces it. This fact is governed by the unbreakable laws of thermodynamics but often seems to be ignored by people proposing cars the run on 'water' or 'Brown's gas' (a mixture of H₂ and O₂ produced by electrolysis [1879]). Generating hydrogen by electrolysis is only (optimally) about 60% efficient (~500 kJ mol⁻¹) and the use of this hydrogen in a car is (optimally) also only about 60% efficient (~172 kJ mol⁻¹), so two thirds of the energy required is wasted. The only time excess energy may apparently be produced (on a laboratory scale) is when the electrodes themselves react; a important factor when using some stainless steel electrodes but often ignored.

An alternative source of energy in water electrolysis has been proposed [1875]. It involves 'cold fusion' ([low energy nuclear reactions](#)), a highly controversial theory developed from experiments involving electrolysis of heavy water using palladium (Pd) cathodes and reportedly producing greater heat than could be conventionally explained. This idea has so far received only limited acceptance with the main criticism being a lack of a suitable theoretical basis. History will decide.

Footnotes

^a **Redox processes.** In oxidation-reduction reactions, the ability to donate or accept electrons is given by the redox potential, E . Here, E^\ominus is the standard (electrode, reduction or redox) potential at 298 K, the measure of individual potential of the reversible electrode at standard state, which, in this case is 1 M and gases at a pressure of 101,325 Pa. $E^{\ominus'}$ is this standard potential but at pH 7.0.

At each electrode the (electrode) potential is given by the **Nernst** equation,

$$E_{\text{electrode}} = E^\ominus + \left(\frac{RT}{nF}\right) \ln \left\{ \frac{[A_{\text{surface (oxidised)}}]}{[A_{\text{surface (reduced)}}]} \right\}$$

A positive redox potential indicates ability to accept electrons (i.e. it is an oxidising agent) and a negative redox potential indicates ability to donate electrons under those conditions (i.e. it is a reducing agent). The electrode potential cannot be determined on its own but only as part of a cell containing two electrodes, where the overall potential is the sum of the individual electrode potentials. Within the cell, negative electrons are passed from the electrode of lower (more negative) E (cathode) to the electrode with a more positive E (anode); and these electrons are then returned via the external circuit. The redox potentials are related to the Gibbs free energy (ΔG) by:

$$\Delta G = -nFE$$

where F = **faraday** ($96,485 \text{ J V}^{-1} \text{ mol}^{-1} = 96,485 \text{ C mol}^{-1} = 96,485 \text{ A s mol}^{-1}$), n = number of electrons transferred

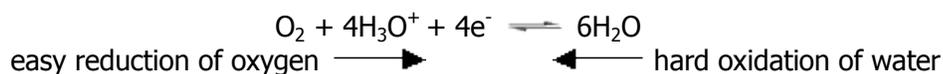
and E is the net redox potential (working cell potential in volts), related to the conditions by the **Nernst** equation

$$E = E^{\ominus'} + \left(\frac{RT}{nF}\right) \ln \left\{ \frac{[A_{\text{oxidised}}]}{[A_{\text{reduced}}]} \right\}$$

where the $[A_{\text{oxidised}}]$ and $[A_{\text{reduced}}]$ terms refer to all the concentration terms (multiplied) in the equation.

Consider $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O} \quad \Delta G^{\ominus'} = -474.3 \text{ kJ mol}^{-1}$

The half reactions are: (the electrons (e^-) are from an electrode)



$$E = +1.229 \text{ V} + \left(\frac{8.314 \text{ J K}^{-1} \times 298 \text{ K}}{4 \text{ mol} \times 96,485 \text{ J V}^{-1} \text{ mol}^{-1}}\right) \ln \left\{ \frac{[\text{O}_2] \times [\text{H}_3\text{O}^+]^4}{1^6} \right\}$$

therefore at pH 7 and unit activity oxygen, $E^{\ominus'} = +1.229 \text{ V} + 2.303 \times (-7) \times 0.0257 \text{ V} = +0.815 \text{ V}$

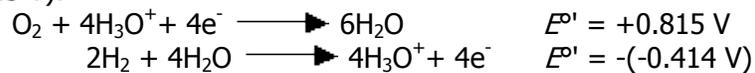


$E^\ominus = 0.00 \text{ V}$ (the standard hydrogen electrode; exactly zero by definition)

$$E = 0.00 \text{ V} + \left(\frac{8.314 \text{ J K}^{-1} \times 298 \text{ K}}{2 \text{ mol} \times 96,485 \text{ J V}^{-1} \text{ mol}^{-1}}\right) \ln \left\{ \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_2] \times 1^2} \right\}$$

therefore at pH 7 and unit activity hydrogen, $E^{\ominus'} = 0.00 \text{ V} + 2.303 \times (-7) \times 0.0257 \text{ V} = -0.414 \text{ V}$

Noting that a compound with the more positive potential will oxidize the reduced form of a substance of lower (more negative) potential., then electrons flow from negative potential to positive potential. In this example, the electrons flow from the hydrogen ($E^\ominus = -0.414 \text{ V}$) to the oxygen ($E^\ominus = +0.815 \text{ V}$).



$$\begin{aligned} \Delta G^\ominus &= -nFE^\ominus \\ \Delta G^\ominus &= -4 \times 96.49 \times 1.229 \text{ kJ mol}^{-1} \\ \Delta G^\ominus &= -474.3 \text{ kJ mol}^{-1} \end{aligned}$$

^b Traditionally such equations are written with the electrons on the left-hand-side and the redox potential refers to so directed equations.



Here it is written reversed in order to show how the cell reaction is balanced, as this is the way the reaction occurs.

^c The electrodes should preferably be made from material with high conductivity, resistance to corrosion and erosion during the electrolysis and able to catalyse the electrode reactions. Also for industrial use, they should be relatively inexpensive. Platinum is an excellent but expensive electrode material. Industrial cathodes may be made from steel or nickel and those used as anodes are metals such as titanium coated with the oxides and mixed oxides of metals such as nickel and cobalt.

Source: <http://www1.lsbu.ac.uk/water/electrolysis.html>