Electrolysis

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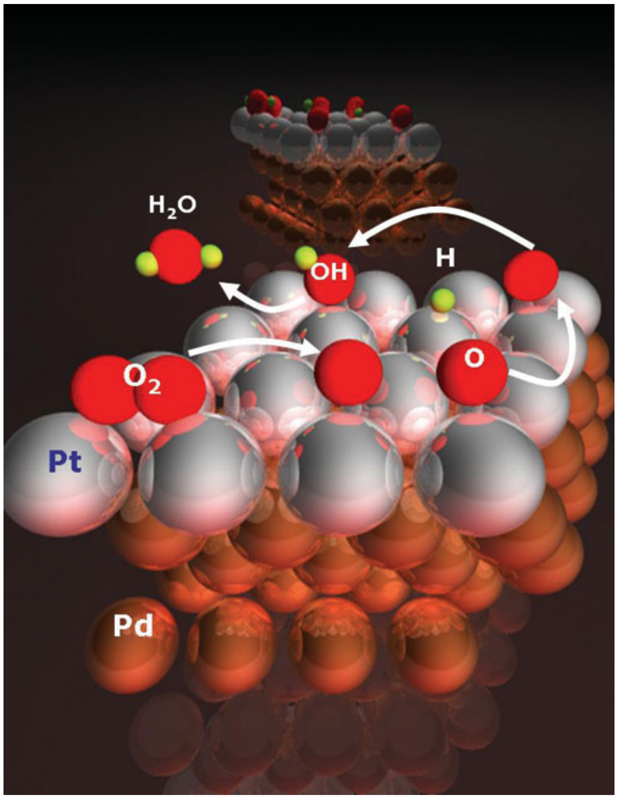

http://www.isgtw.org/images/fuel.jpg

University Physics 2

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Due Date: November 29, 2010

Introduction

Electrolysis is a separation technique that uses direct electric current through an ionic substance to drive a non-spontaneous chemical reaction. The basic principles of electricity and those of conductive materials are what drive the electrolysis process. Electrolysis is valuable in chemistry and industry in the separation of elements. Usually electrolysis is set up in a cell composed of an energy source that supplies direct current, an electrolyte, and two electrodes. The electrolyte must contain free ions in order to carry electricity throughout the solution. Electrons carry the direct current in the external circuit and supply the necessary energy to discharge the ions. The electrodes serve as an interface between the electric circuit providing the energy and electrolyte. Usually the desired products from electrolysis are in a different physical state than the electrolyte so another process is needed to collect the products.

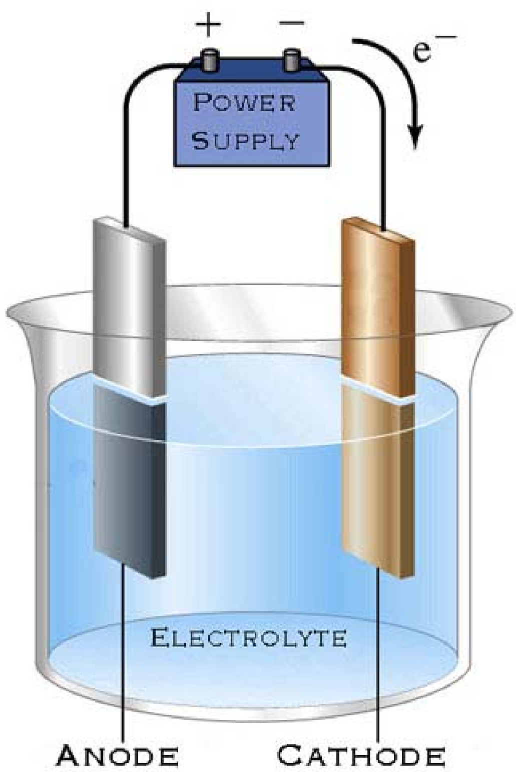
Electrolysis is essentially based on Faraday's first and second law of electrolysis. The principles of electrolysis are used in several chemistry and industrial processes such as electrophoresis, electrometallurgy, anodization, electroplating, and the production of several chemicals/elements such as trifluoroacetic acid, chlorine, sodium chlorate, aluminum, lithium, sodium, potassium, and magnesium. Current research has posed electrolysis as a potential process that could produce large amounts of hydrogen and help meet the increasing energy demands. As a plus the energy produced would come from water which is a renewable source. This process could potentially decrease the current dependence on hydrocarbons as a source of energy. The wide use of electrolysis makes this technique important and a more careful study of how it works and the challenges it faces will help understand what needs to be done in order to make this process the supplier of tomorrow's energy.

Background

The electrolysis cell has two electrodes immersed in an electrolyte solution that has an electric potential applied across. The "electrolytic conductors" (Kuhn 1971) can function in acids, bases, salts, fused salts, some solid substances, and hot gases. The electrodes are basically plates that are made up of good electric conducting metal material such as aluminum, nickel, copper, magnesium, etc. The negative electrode is known as the cathode and the positive is the anode. The source of electricity comes from a battery which supplies the energy needed to move ions from one electrode to another. The movement of the current is associated with a movement of matter. When the current leaves the electrolyte, it cannot take the matter with it; so it is set free. The movement of matter by electricity causes each electrode to attract ions that are opposite in charge and the principle of "opposites attract" applies, so a cation will move towards the negative cathode and an anion will move towards the positive anode.

An example of the principle presented above would be the set up of two platinum plates or wires dipped into dilute sulfuric acid, H_2SO_4. The plates or wires would then be connected either with two poles to a battery or to another source of direct current, which would allow electrolysis to take, place. Let us assume that the desired product from this process is hydrogen. As electrolysis is taking place the platinum plate connected to the negative terminal of the battery produces hydrogen gas. The plate that produces the desired product is also known as the working electrode. The plate connected to the positive pole of the current source, produces the oxygen gas. For electrolysis the products, which for this case are gases, are only produced at the plates and not throughout the path where electricity flows. Membranes or separators are sometimes implemented to the cell to prevent the products from mixing. If exposure to oxygen produces side reactions the container of the cell is modified to prevent the products from being exposed to the atmosphere.

At each electrode electrons are absorbed or released by the atoms and ions (Wikipedia 2010*). The atoms that gain or lose electrons become charged ions and pass into the electrolyte. The ions that gain or lose electrons become uncharged atoms and separate from the electrolyte, this phenomenon is known as discharging. Oxidation-reduction type reactions take place in electrolysis where oxidation occurs at the anode and reduction in the cathode. A picture of an electrolysis cell showing the basic components of the process is presented below in figure 1:



http://www.rustyiron.com/engines/electrolysis/electrolysis.jpg

Figure 1. Electrolysis set up shows power supply, electrolyte, electrodes, anode, and cathode.

Theory

In 1834, Michael Faraday published *Faraday's Laws of Electrolysis* based on quantitative observations he made. Faraday's first law of electrolysis states that "the mass altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at the electrode" (Wikipedia 2010). The mathematical equation of this principle is:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

where m is the mass of the substance released at the electrode, Q is the total electric charge passed through the substance, F is Faraday's constant (96,485 C/mol), M is the molar mass of the substance, and z is the valency number ions of the substance. For this mathematical model M, F, and z are considered to remain constant so the value of m is proportional to the value of Q. The second part of the equation $\frac{M}{z}$ is also known as the "equivalent weight".

Faraday's second law of electrolysis states that "for a given quantity of electric charge the mass of an elemental material altered at an electrode is directly proportional to the elements equivalent weight" (Wikipedia 2010). Faraday's second law of electrolysis is independent of the concentration of the electrolyte and holds true at all temperatures, solvents, solid electrolytic conductors, and molten salts (Mantell 1940). The mathematical model of Faraday's second law of electrolysis is shown below:

$$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right)$$

where n is the amount of moles liberated, Q is equal to I multiplied by t. In the equation Q is replaced by I*t where I represents current, t is the total time the constant current was applied. When the current is not constant the following integration applies:

$$Q = \int_0^t I \, d\tau$$

where current is a function of tau and t is the total electrolysis time.

In order for electrolysis to take place the amount of electrical energy added must equal the change in Gibbs free energy of the desired reaction and the encountered losses in the system. The efficiency of the system is equal to the enthalpy change divided by the free energy of the reaction. Commercial electrolytic cells work around an efficiency of 60-70% (Casper 1978). Usually the electric input is larger than the enthalpy change of the reaction which causes for energy to be lost in the form of heat but this is not always the case. In the electrolysis of steam to form hydrogen and oxygen at high temperature, heat is absorbed from the surroundings so the enthalpy change of the reaction is higher than the electric input.

The Uses of Electrolysis

The basic principles of electrolysis are used for the separation of other elements/molecules in chemistry and industry. The several uses of electrolysis in these fields will be discussed for the following processes; electrophoresis, anodization, electroplating, and the electrolysis of water. To understand the wide use of electrolysis we will go in detail on how these techniques function.

For electrophoresis an electric current is passed through a porous diaphragm immersed in liquid, the flow of liquid through the diaphragm is usually from the anode to the cathode. It was first noted by Reuss, who used clay diaphragms in water, that as the current forced water through the clay a migration of suspended clay particles from the cathode to the anode occurred (Mantell 1940). The migration of the suspended particles is also known as electrophoresis while the flow of liquid is known as electrical endosmose. Electrophoresis is used in the purification of clay in order to remove suspended clay particles, in the manufacturing of chemical stoneware to eliminate laminations, and in gel electrophoresis in order to separate molecules based on size and charge.

Anodization uses electrolysis to increase the thickness of the natural oxide layer on metal surfaces. This process also increases resistance to corrosion and/or adhesion of paint coatings. This process is called “anodization” because the part that is treated forms the anode part of the electrical circuit and it is where the oxidation process takes place. This process is usually applicable to metals such as aluminum, titanium, tantalum, copper, and magnesium. For example the anodization of aluminum takes place in 10-50 wt% sulfuric acid, at 15-20ºC, 1.2 A/dm^2, with a cell voltage of 10-20V, and a coating of 15-20 micrometers should be obtained within 30 minutes (Elsevier 1971) . Depending on how much coating is needed this process can be modified changing the surface exposed, the time, temperature, and changing the concentration of the solution used.

Electroplating uses electrolysis to produce metallic coatings on base metals and to an extent on nonmetallic articles. During the process the object must be free of any scales and grease so pre-treatment is needed before electroplating is conducted. For this process the metal that will be deposited onto the base metal is present as ions in the electrolyte in the anode part of the electrolysis cell. The ions of the metal are then discharged on to the base metal being plated which is also known as the cathode. These coatings are very thin layers of some other metal or metals applied over the base metal. The success of this process depends on the composition of the electrolyte and the operating parameters such bath temperature, cathode, and anode current density, pH of electrolyte, agitation, etc. (Kuhn 1971). The uniformity of the metal distribution relies heavily on the relationship between the cathode polarization and the electrical conductivity of the electrolyte.

Electroplating is utilized for the following; decorative purposes, increasing corrosion resistance, and to lengthen the industrial life of base metals. This process can also give base metals specific properties like hardness, wear resistance, anti frictional properties, electrical, and magnetic properties. The base metals are usually cheap metals and this process allows the use of these metals in environments that would not be possible without electroplating, environments such as strenuous industrial conditions and even the atmosphere.

The typical water electrolysis cell is composed of nickel plated mild steel electrodes immersed in a 30% potassium hydroxide, KOH, aqueous solution, a woven asbestos cloth separator, and direct current is passed through the cell to produce both hydrogen and oxygen. The chemical reaction that takes place in the cathode is the following:

$$2\,H_2O + 2\,e \rightarrow\; H_2 +\; 2\,OH^-$$

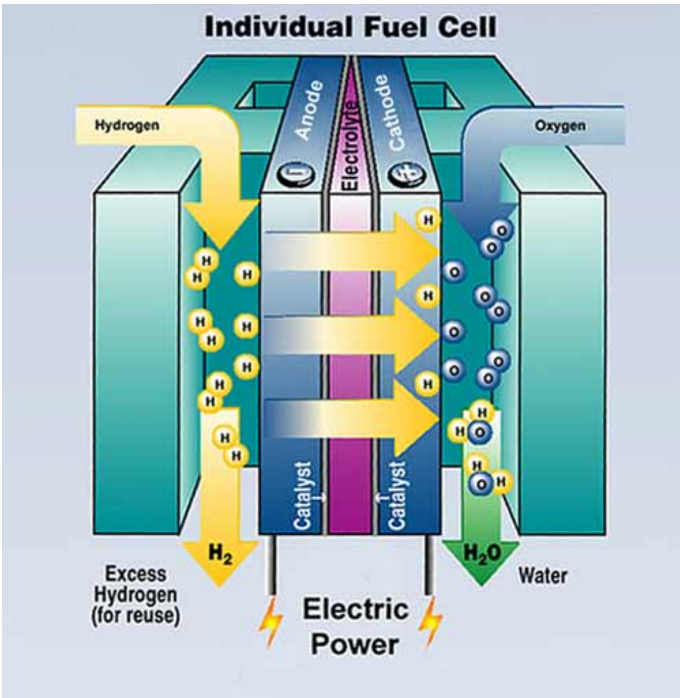
where hydrogen molecules accumulate on the surface of the cathode and are discharged to the surface of the electrolyte. Meanwhile, in the anode the following chemical reaction takes place:

$$2\,OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2\,e$$

As the process continues water is removed from the solution and more water needs to be supplied. The woven asbestos separator is used to prevent oxygen and hydrogen gases from mixing together. The hydrogen gas produced through this process is about 99.9% pure. The addition of gas exit pipes is necessary at the cathode and anode in order to collect the newly produced gases. About 30-40% of the energy supplied to the cell is used up to drive the electricity up through the cell and is dissipated as heat.

The advantage of a water electrolysis is that it uses water as a feed, it is not labor intensive, and would use up a small amount of space if a commercial plant was built. The average efficiency of this process is about 60% and can be increased by operating at higher temperatures and pressures. The biggest challenge is overcoming the resistance to electricity and other losses encountered in electrolysis cell (Casper 1978). Water electrolysis and the reverse of this process also known as the hydrogen fuel cell has become of interest to many energy researchers.

The hydrogen fuel cell generates an electric current by catalytically oxidizing hydrogen which produces water and some heat, and has created hope that hydrogen could be the fuel of tomorrow's energy. A figure is shown below which demonstrate an example set up of this cell.



http://specialnewsonline.files.wordpress.com/2009/10/fuel-cells.jpg

Figure 2. Hydrogen fuel set up.

The hydrogen fuel cell can operate continuously if the reactants and the oxidant needed are maintained which makes this process ideal. Before the hydrogen fuel cell is implemented permanently in the transportation industry and in energy generation applications the problems encountered with low process efficiencies and tremendous losses of energy in heat must be solved. A feasible manner on how to provide hydrogen to the cell must also be discovered.

Conclusion

The basic physical principles of electrolysis and its set up are very simple but the actual problems encountered are very complex. The importance of electrolysis can be deduced from its various different applications in industry for processes such as in electrophoresis, anodization, electroplating, and the hydrolysis of water. In addition, electrolysis is also used in the production of important chemicals and elements such as trifluoroacetic acid and chlorine which is used as a household cleaning product to kill bacteria and in the purification of water. Electrolysis is also used in the recovery of metals such as aluminum, lithium, and magnesium to name a few so that they can be used in other important processes. Currently chemical and pharmaceutical industries utilize electrolysis in their processes.

The establishment of electrolysis as a reliable process has led many to believe that its ability to produce considerable amounts of hydrogen through water electrolysis holds the key to solving the expected energy shortage problems in the future. Fossil fuels have been highly relied on to meet current energy demands but the fact that there is a short supply of fossil fuels has created a problem. Indeed this form of hydrogen production does originate from a renewable source but in order for this process to become competitive with other current methods of hydrogen production available in the market it must present comparable operating costs. Currently it is the most expensive method of hydrogen production in the market and that is its major drawback. According to the book *Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques* the most economically sound solution will be the use of both hydrogen and electricity to this energy crisis.

Overall all current processes that utilize electrolysis have the potential to be optimized by finding better electrode materials that have lower electricity resistance and materials that can perform comparably or better than the ones used currently and can function at higher temperatures and pressures. These changes would decrease the loss of energy through heat and increase the electrolysis cell efficiency. For most electrolysis processes operating at higher temperatures and pressures would increase efficiency but it would shorten the lifespan of the materials used to conduct the desired reaction which is not economical. This is one way to decrease operating costs and one other major factor would be to find a cheap way to supply electricity to the cell which some researchers have suggested that in the future this could be obtained from hydropower, solar, nuclear, or geothermal energy (Casper 1978).

Bibliography

Brus, David, and Doug Hotek. 2010. "Exploring Hydrogen Fuel Cell Technology." *Technology Teacher* 69, no. 6: 20-24. *Academic Search Premier*, EBSCO*host* (accessed September 27, 2010).

Daniel C Harris, Quantitative Chemical Analysis, New York: W.H. Freeman and Company, 2007, 7^{th} edition, 270-328.

Industrial Electrochemical Processes. A.T. Kuhn. Amsterdam: Elsevier Publishing Company, 1971.

Mantell,C.L.. *Industrial Electrochemistry*. 2 ed. *Chemical Engineering Series.* New York: McGraw-Hill Book Company, Inc., 1940.

*Wikipedia contributors, "Electrolysis," *Wikipedia, The Free Encyclopedia,* http://en.wikipedia.org/wiki/Electrolysis (accessed November 28, 2010).

Wikipedia contributors, "Faraday's laws of electrolysis," *Wikipedia, The Free Encyclopedia*, http://en.wikipedia.org/w/index.php?title=Faraday%27s_laws_of_electrolysis&oldid=394674628 (accessed November 29, 2010).

Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques. M.S. Casper. Park Ridge, New Jersey: Noyes Data Corporation, 1978. 7, 111-192