Discovering the principle of the fuel cell at home or in school

Introduction

Fuel cells convert chemical to electrical energy. Engines and turbines with generator can also do this but there is a lot more interest in fuel cells. It is reported that the latter have a much higher efficiency than internal combustion engines and that the future of energy supply is unthinkable without them. In cars, houses and wherever energy is required, they will be found in future in the same places and numbers as car engines and single-storey heating are found today.
If this is true I think everyone should be better informed about this matter.

About the author

Dr. Martin Schmidt is a physicist and was head of marketing and sales with a company that develops, manufactures and sells fuel cells. Of course he was often asked how fuel cells actually work. He likes to answer such questions with an experiment, but it irritated him that commercially available kits are expensive and uninstructive.

While studying historical reports he had the idea of reproducing the experiments of fuel cell pioneers with very simple apparatus in order to make the principle of the fuel cell comprehensible. It was really simple but nevertheless most instructive, and he considered that everybody who is interested in fuel cells should be in a position to reproduce this experiment and understand it. In this way the idea arose to create a website on the subject and to offer on it the only components that are are not readiy available, the two platinum electrodes.

Objective

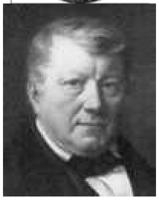
In the following the principle of the fuel cell will be explained in a simply way that will be understood by everyone. We shall focus only on the basic electrochemical phenomena and not on today's technical applications, about which one can read on numerous websites. The instructions are written for all interested persons, even for those having little prior knowledge of the subject. Even if it may appear somewhat long-winded to the specialist: please read everything first before experimenting!
A key objective is naturally to build oneself a fuel cell, originally referred to as a "gas battery". For this purpose, two platinum wires are needed which act as electrodes. All other ingredients will be found in the kitchen cupboard, tool-box or supermarket. This fuel cell is too weak to drive a lamp or motor. All effects will only be seen on a voltmeter: they appear as quite a high voltage of about 1.4 V, i.e. they are easily detectable. The small power output is a result of the low surface area of our platinum electrodes. If you have larger quantities of platinum lying about at home, you can reproduce the small gas battery described here on a larger scale. It will certainly work but will be extremely expensive. In this case, we would rather advise you to buy a kit containing a higher power fuel cell which, however, will be quite uninstructive since one cannot see how it works. Teachers who want to deal with the fuel cell in physics or chemistry classes will want to have both: a small gas battery for eperimentation by the pupils and a professional fuel cell that can do more work than just operate a voltmeter.

In the tracks of the researchers

In the second half of the 18th century and during the entire 19th century, scientists were fascinated by the phenomena and possibilities of electricity. Quite early on already, researchers saw and described effects which were to become the foundations of fuel cell development. Among the pioneers were:

Alessandro Volta, Pavia
1745-1827

Johann Wilhelm Ritter, Jena
1776-1810



Christian Friedrich Schoenbein,
Basel
1799-1868

William Robert Grove, Oxford
1811-1896

Volta was the first to place the observations of the electrical phenomena on a scientific footing. Ritter continued to develop the understanding of electricity up to his early death in numerous experiments and today is considered to be the founder of electrochemistry. Schoenbein and Grove, who became friends through their exchange of experiences, systematically researched what we nowadays refer to as fuel cells. At that time they were still called gas batteries. This term is highly instructive and describes the fundamental principle much better than the abstract designation fuel cell.
The experiments which Schoenbein conducted in the summer of 1838 in his institute at the University of Basle can be easily understood and reproduced. The effects are strong and clearly visible, and various sources report that Ritter had seen them too. However, at that time the most sensitive measuring instruments were freshly prepared frogs' legs, one's own tongue or one's finger. Ritter reported in February 1801 on experiments in which he exposed himself to frequent, intense electrical shocks. Afterwards he felt ill, had to stay in bed for several days and even after 10 days did not feel well again. No wonder that he no longer overloaded his "measuring instrument". Today we have a much easier time. We no longer have to collect fresh frogs at dawn for our experiments or risk our own health, but can buy inexpensive, highly sensitive digital multimeters in the hobby section of a supermarket.
In the following we shall approach the subject in simple steps.

Step 1: Understanding electrolysis

Fundamentals

Electrolysis, known at that time as "splitting of water", was especially fascinating to the researchers. An electrolyte is a substance in which ions are present, in our case a solution in water. This can be an acid, alkali or salt solution. Ions are charged particles that occur under the influence of the polar water molecules, a process known as dissociation. Metals and hydrogen form positive ions, non-metals form negative ions. The following table shows examples.

Substance in solution	Name	Positive ions (cations)	Negative ions (anions)
H_2SO_4	sulphuric acid	H^+, H^+	SO_4^{2-}
NaOH	caustic soda	Na^+	OH^-
NaCl	common salt	Na^+	Cl^-

To carry out electrolysis it is necessary to introduce two similar electrodes into the solution. They are connected to the poles of a source of direct current (DC, e.g. a battery). The positively charged ions (cations) migrate to the minus pole, also known as the cathode. The negatively charged ions (anions) move to the plus pole (anode). On the electrodes the ions are discharged and are then present as neutral particles (atoms or molecules). In this form they react with the chemical environment: they precipitate on the electrode, escape upward as a gas or are involved in secondary reactions. This will be illustrated by an example.

An important example

In the following a solution of common salt is always assumed, it being most easily prepared and harmless. Common salt (NaCl), dissolved in water, dissociates to sodium ions and chloride ions (Na^+ and Cl^-). Cl^- migrates to the positive electrode (anode), is discharged (give up an electron) and forms gas molecules (Cl_2), which rise to the surface as small bubbles. One can smell the chlorine gas (as in a swimming pool with chlorinated water). Na^+, on the other hand, migrates to the negative electrode (cathode) and is discharged there (takes up an electron). Sodium, a highly reactive metal, is unstable in water and is immediately converted in a secondary reaction to sodium hydroxide (NaOH). For this to happen, an OH^- ion must be torn from the water (H_2O), leaving an H^+. The H^+ ions join to form hydrogen molecules, which rise at the cathode as small bubbles. The reaction products of the electrolysis of common salt solution are hence chlorine gas (Cl_2) and hydrogen gas (H_2).

Step 2: From electrolysis to the gas battery

When one removes the external voltage source from our electrolysis experiment, the effervescence of the rising gas bubbles stops but many of them are left sticking to the electrodes. J. W. Ritter is accredited with the observation that an electric voltage could be measured on such a cell after the external voltage had been detached. The fact that gas-covered electrodes can supply electricity is nothing other than the fuel cell effect. One can also call it a gas battery or reverse electrolysis, or a special kind of galvanic element.

Schoenbein carried out such experiments in 1838 in a systematic manner, interpreted them correctly and published his results for the first time in January 1839 in the Philosophical Magazine. The elements that produced electricity in his experiments were the electrode pairs hydrogen/chlorine and hydrogen/oxygen. Hence we are actually following in the footsteps of the fuel cell pioneers! Let us look at the situation more closely.

Step 3: Understanding galvanic elements

In the simplest case a galvanic element consists of the arrangement
ANODE - ELECTROLYTE - CATHODE.
Such elements allow chemical energy to be converted into electrical energy.
The best-known case is when anode and cathode are of different metals, e.g. copper (Cu) and zinc (Zn). The base metal, in this case Zn, corrodes: positively charged Zn^{2+} ions go into solution, leaving electrons at the Zn electrode (which becomes a minus pole). When Zn^{2+} ions precipitate on the Cu electrode, they need 2 electrons for discharging. Hence there occurs a deficiency of electrons on the Cu electrode (which becomes a plus pole). Such an electrical inbalance must be corrected. The electrons would prefer to migrate in a direct path from the minus pole through the electrolyte to the plus pole, but an electrolyte conducts only ions and not electrons, i.e. is an insulator for the latter. These must therefore make the detour around an external circuit (and perform work for us) before the charges can be equalized.

The spontaneous (exothermic) corrosion reaction of the zinc thus provides us with electrical energy. All the batteries we use in portable electrical or electronic appliances work basically according to this principle.

Step 4: The gas battery as a galvanic element

But why does our gas battery work? We do not have different electrode materials and hence no voltage should appear! This objection would be perfectly correct, were there not to be gas bubbles on the electrodes as a result of the electrolysis. In our example of a salt solution, we in effect have a chlorine and a hydrogen electrode, i.e. different electrodes. here we see a further important point: the chemistry takes place not in the electrode but exclusively at its surface.

Step 5: The gas battery as reverse electrolysis

On the gas-covered electrodes and in the electrolyte solution, the reverse reaction to electrolysis takes place. As a result of the electrolysis, hydrogen and chlorine gas are present. These recombine to form hydrochloric acid (HCl), a synthesis. Here, however, we must observe an important restriction: this reaction can only take place when platinum electrodes are used. Without the catalytic effect of the platinum surface, this reaction cannot proceed spontaneously (exothermally) at room temperature. The scientific term here is heterogeneous catalysis.

Instructions for experimentation

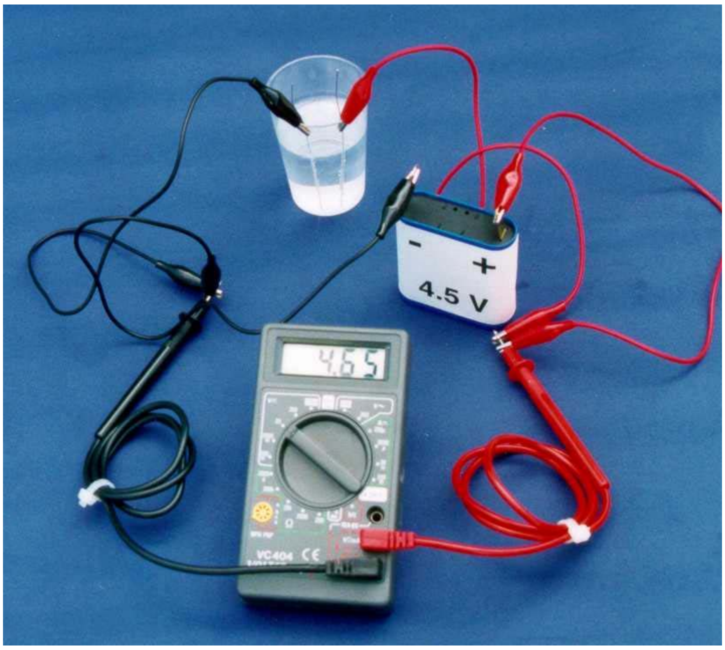
Apparatus

- one small glass with water and a knife-tip of common salt
- one high impedance voltmeter with ranges of 0-2 VDC and 0-20 VDC (an inexpensive digital multimeter from the hobby section of a supermarket will suffice; an old needle instrument will also do, but the effects will be seen less clearly)
- one 4.5 volt battery
- experimental cables, preferably with small crocodile clips (the resourceful experimenter can do without these cables but they are easier to work with)
- 2 platinum wires as electrodes

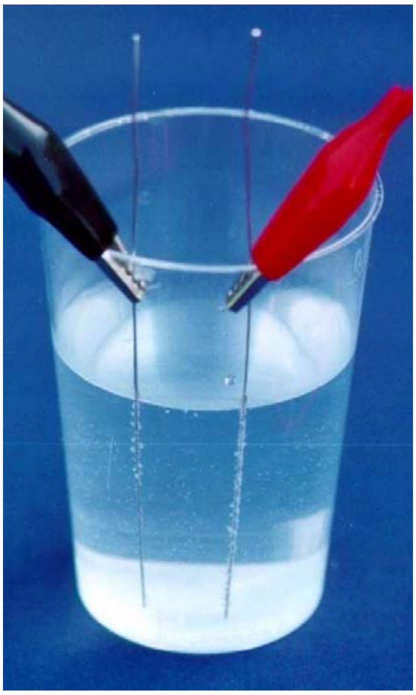
Experimental procedure: electrolysis and gas battery

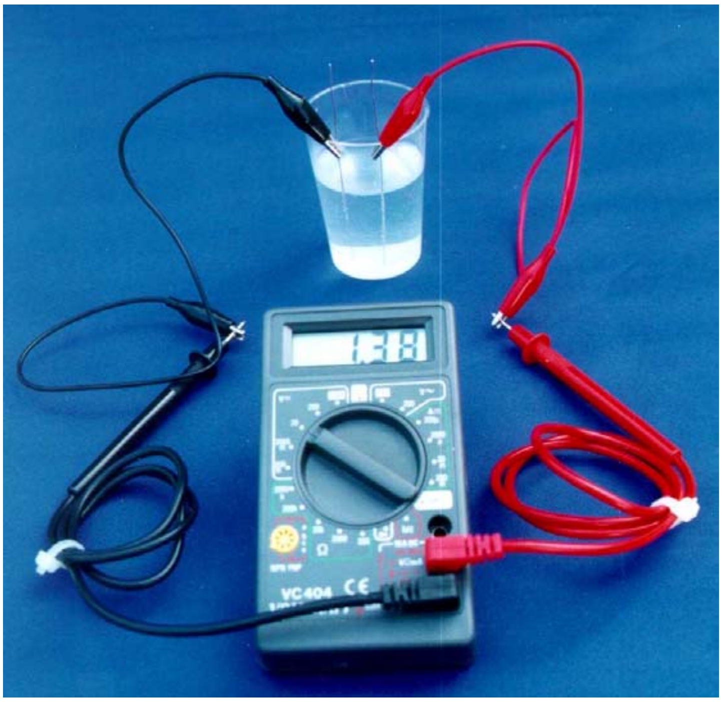
- A knife-tip of common salt is dissolved in water in a small vessel (glass or plastic). The solution is turbid at first but will become clear after a while (better for observing what happens at the electrodes).
- The two platinum wires (electrodes) are fixed at the edge of the glass (preferably by means of the crocodiles clips on the cables). The platinum electrodes should not be too far from each other (a few millimetres is ideal), but should not touch.
- The platinum electrodes are connected to the voltmeter (polarity is unimportant). The very first time one will measure no voltage, even in the most sensitive VDC range (except for small effects from stray electromagnetic fields). On repetition of the experiment, however, the electrodes may be no longer identical (adsorbed traces of gas from the previous experiment) and one can already see very small effects.

- The voltmeter is switched to the 0-20 VDC range and the battery connected to the platinum electrodes (plus to plus, minus to minus pole). One observes vigourous gas evolution at the electrodes (the chlorine gas can be smelt when close enough). The gas mixture is in principle explosive but the small quantities make the experiment harmless. The voltage of the battery is measured on the voltmeter (between 4 and 5 V).



- The battery is disconnected, preferably without shaking the glass so that as many gas bubbles as possible remain adhered to the electrodes. Now we have no more electrolysis but the voltmeter still shows a voltage of about 1.4 V which slowly sinks (switch voltmeter to a more sensitive range as needed). Our cell now functions as a gas battery or fuel cell! It is true that it cannot drive anything other than a voltmeter, but the effect is clearly observable (for higher power, e.g. to drive a lamp or motor, one needs larger vessels and greater electrode areas).





- By reconnecting the battery for a short time (after switching the voltmeter to a suitable range), one can recharge the gas battery as often as desired and repeat the experiment.

Experimental procedure: modification

- Acids and alkalis may also be used as the electrolyte (e.g. sulphuric acid, hydrochloric acid or caustic soda) but this is dangerous because of the caustic nature of the substances. Don't do it! The effects are not stronger than with the simple "common salt fuel cell". Instead try out some unusual electrolytes like orange juice or vinegar. These organic acids are admittedly rather weakly dissociated electrolytes but one still sees a clear, if rather weaker, effect.

Experimental procedure: control experiment

- It was stated above that the catalytic effect of the platinum is a prerequisite that the fuel cell can function at all. This can be proven by using electrodes having no catalytic effect. These could be straightened paper-clips in the simplest case, but leads from refillable pencils are ideal because they do not enter into any reactions whatsoever with the electrolyte or the reaction products. Repeat the experiment with such electrodes (caution, they are fragile). One then sees evolution of gas at the electrodes as before, but after disconnecting the battery the voltage is only very small. It is still a galvanic element but not a gas battery or fuel cell. The changes to be seen in the short-time, very low voltage are changes in the chemical environment of the electrodes: at the minus pole, as already explained, a little caustic soda (NaOH) is formed and hence slightly changed local conditions arise. This effect also occurs, by the way, at the platinum electrodes but it is masked by the much stronger fuel cell reaction.

Theory

Introduction

Actually one could discover and explain the whole of electrochemistry through these simple experiments, but we shall not go that far. A few fundamentals of basic electrochemical processes will nevertheless be mentioned.

Electrolysis

Anodic reactions	
Electron release (oxidation)	$Cl^{-} -> Cl + 1 e^{-}$
Formation of chlorine (gas) molecule	$2 Cl -> Cl_2$
Overall reaction	$2 Cl^{-} -> 2 e^{-} + Cl_2$

Cathodic reactions	
Electron acceptance (reduction)	$Na^{+} + 1 e^{-} -> Na$
Secondary reaction: formation of caustic soda	$Na + H_2O -> NaOH + H$
Formation of hydrogen (gas) molecule	$2 H -> H_2$
Overall reaction	$2 Na^{+} + 2 e^{-} -> 2 NaOH + H_2$

Fuel cell reaction

This is practically the reverse reaction to electrolysis, the synthesis of hydrochloric acid. In the following, the overall reaction, partial reactions and standard potentials E^0 of the redox pairs H_2/H^+ and Cl_2/Cl^- are given.

Overall reaction	$H_2 + Cl_2 -> 2 HCl$	
Electron acceptance (reduction)	$Cl_2 + 2 e^{-} -> 2 Cl^{-}$	$E^0 (Cl_2/Cl^-) = 1.36$ Volts
Electron release (oxidation)	$H_2 – 2 e^{-} -> 2 H^{+}$	$E^0 (H_2/H^+) = 0$ Volt (by definition)

The standard potentials are defined for normal conditions (normal pressure, room temperature, activities = 1). However, one usually works under other conditions in a free experiment, particularly with concentrations not corresponding to an activity of 1 (i.e. in an approximately 1 molar solution). This leads in practice to somewhat different electrochemical potentials or voltages between the electrodes.
If one were to conduct the experiment with the redox pairs H_2/H^+ and O_2/O^{2-}, the classic synthesis of water from its elements, one would obtain a voltage of 1.23 V.
On close observation, one sees initially after disconnecting the battery a higher voltage than can be explained by theory. It is about 2 V but very quickly drops to the expected value of 1.4 V. The probable explanation is that the cell has a certain electrical capacity, as with a capacitor, that is able to store a part of the electrical charge from the battery for a short time. It thus has nothing to do with the fuel cell effect.

The end result of all chemical reactions

By the way: you may have found it disturbing that we started from a common salt solution but ended up with hydrochloric acid, i.e. complete reversibility is not obtained. This is, however, not the end of all the reactions in our cell: since caustic soda was formed during the electrolysis, the following neutralization reaction will occur after the fuel cell reaction (HCl synthesis):

$$NaOH + HCl -> NaCl + H_2O$$

The end result is finally common salt and water, the starting products. In practice, the equation will not be balanced exactly since during electrolysis bubbles of chlorine and hydrogen will be lost, and the remaining gas is not reconverted fully during the fuel cell reaction. But in theory a closed system is possible in which the sum of the starting products equals that of the end products.

Ecological aspects

Note 1

Our experiment is simple and instructive, but does not make ecological sense at all. A battery, in which chemical energy is converted to electrical energy, is used to charge our gas battery and at the end we obtain electrical energy again. But if we imagine obtaining the electrical energy to charge the gas battery from wind power or a photovoltaic system, then sensible applications of the gas battery alias fuel cell can be devised. We should then be dealing with a fuel cell that converts hydrogen. There exist many ideas, in some cases experimental projects, on the subjects of hydrogen generation and storage, and naturally on fuel cells.

Note 2

There are different types of fuel cells that are distinguished by the type of electrolyte material and hence the operating temperature. Not all require as a fuel pure hydrogen, which is extremely demanding with respect to generation, transport and storage. The higher the operating temperature, the less critical is the question of the fuel. High temperature fuel cells can be operated with natural gas or biogas without much trouble. The higher the temperature, the less dependent one is on the participation of (usually very expensive) catalysts in the basic chemical reaction. On the other hand, high operating temperatures place very high demands upon the materials used, which is why only highly specialized companies can offer feasible concepts and systems. Pioneer work in this field has been done especially by Siemens-Westinghouse (USA) and Sulzer Hexis (Switzerland). In the (probably long) transition time to a hydrogen economy, this type of fuel cell in particular is considered to be of great importance.

Note 3

Electrical energy is frequently generated by large power stations fuelled by fossil fuels. In this process, a large part of the fuel energy appears as unused waste heat. This is unsatisfactory because the waste heat also represents the consumption of primary energy and hence the generation of CO_2. If one complements this situation with stationary, decentralized systems that generate a part of the electrical energy in the household itself, the waste heat can be utilized in a sensible manner. If one does not use the waste heat (e.g. for the production of hot water), then the ecological advantage of a decentralized system disappears. For this reason, some European countries prohibit the use of decentralized system in residences merely for electricity generation. Stationary fuel cell systems that can be operated with natural gas or heating oil have great advantages for this application: high efficiency, silent operation and low maintenance and emissions.

In media such as the Internet one can find an increasing number of references to this subject.