Water Splitting and Real World Hydrogen Use

From Photochemical Cells to Steam Reforming

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Abstract

Hydrogen is used industrially in several occasions. It is widely used for petroleum refining and to make industrial commodities such as ammonia. A potential use for it as well is as a fuel, but it isn't widely used due to its price and efficiency. In this paper, I will talk about two methods of obtaining hydrogen: water splitting and steam reforming. Water splitting, though, is not a method. Many methods and procedures can be categorized as water splitting. I will explain some of these methods, compare them and talk about their advantages and disadvantages. Also, I will talk about experiments run by me during my fieldwork. I attempted replicating a few variations of water splitting, by using solar panels as the source of energy, and by using batteries. I also used different conductors and solutions to compare their efficiencies and effects on the final result of the reaction.

Introduction:

Water splitting is a technique where the water molecule is split in order for its components to be separated, H_2 (hydrogen gas) and O_2 (oxygen gas). This way, hydrogen can be used an alternative energy source and also as an environment-friendly fuel, as well as a highly valuable industrial material that can be used for future production of other chemicals and for the refinement of several materials. Water splitting, however, is not a method. There are multiple methods that can be categorized as water splitting. The challenge behind it, though, is that most methods are not economically viable. Usually, the majority of those methods are highly energy consuming, meaning that the energy put into the reaction is more valuable and expensive than the hydrogen product itself. Electrolysis, for example, is the technique of having an electric current pass through the water. It will consume large amounts of energy to split water at low efficiency, about 4%. Among other methods are photoelectrochemical water splitting, also known as artificial photosynthesis. The main idea of this method is similar to electrolysis, but the energy is obtained by using a photoelectrochemical cell - a cell that transforms solar energy into electricity, such as a solar panel. Photocatalytic water splitting is quite similar to photoelectrochemical water splitting, but this method uses a catalyst to increase the efficiency by decreasing the activation energy of the reaction (amount of energy needed for the reaction to happen). Even though photocatalytic water splitting doesn't consume as much energy and its efficiency is significantly higher, it still doesn't make the production of hydrogen as a fuel viable, for the cost is still high and its efficiency low.

Despite my project focusing heavily on water splitting, there are also other ways of obtaining hydrogen. Nowadays, one of the most widely utilized way of getting H_2 is by extracting hydrogen gas from natural gases (such as methane), a method called steam reforming. The steam reforming method requires a metal-based catalyst and extremely high temperatures (800-1100 °C), and it yields hydrogen at a high efficiency (up to 80%). However, this method isn't environment-friendly, as CO_2 is also a product of the reaction. There are methods being researched of how to collect the CO_2 and reuse it to obtain energy.

In this paper, I will discuss different methods of water splitting, as well as briefly discuss some advantages and disadvantages of steam reforming. I will, also, talk about the use of hydrogen as a fuel and how that might become a viable option in the real world, as well as my fieldwork and what I learned and observed from the experiments I ran.

Oxidation:

Before we go over into the methods and the chemistry itself, I would like to briefly go over oxidation, for it is one of the biggest issues and most crucial parts in this topic. It might be an issue when it happens to conductors/semiconductors in many cases. However, some catalysts might rely heavily on oxidation for them to be efficient, as we will get into more detail later.

Oxidation is when an atom loses electrons. When a metal is oxidized, it forms what is called a metal oxide, commonly known as rust. Even though rust is technically only iron oxide, other metal oxides might be popularly also referred to as rust. Since metal oxides have no free electrons to allow electricity to pass through them freely, they don't conduct electricity.

If a copper wire is used as an electricity conductor for splitting water, the wire would oxidize due to the contact with O_2. Since copper oxide doesn't conduct electricity nearly as well as pure copper, the reaction wouldn't be nearly as effective as it would be in case the copper didn't oxidize.

Water splitting (electrolysis/photochemical cells)

The water molecule is composed of two hydrogen atoms and one oxygen atom. The molecule is L-shaped, with the oxygen in the middle and hydrogen atoms on each side, forming two bent bonds. Since the bond between the hydrogen and the oxygen is a covalent bond (intramolecular bond formed when a nonmetal is bound to a metal), a lot of energy is needed for this bond to be broken. We say its activation energy - amount of energy needed for a reaction to happen - is quite high. 463 kJ/mol. For that reason, we use a catalyst. Catalysts are other chemicals used with the purpose of finding a “shortcut” to the reaction, meaning that they lower the reaction’s activation energy.

Since water splitting is an endergonic process – it absorbs energy to be able to break the OH bonds - we need a catalyst that would lower the amount of energy needed to break this bond.

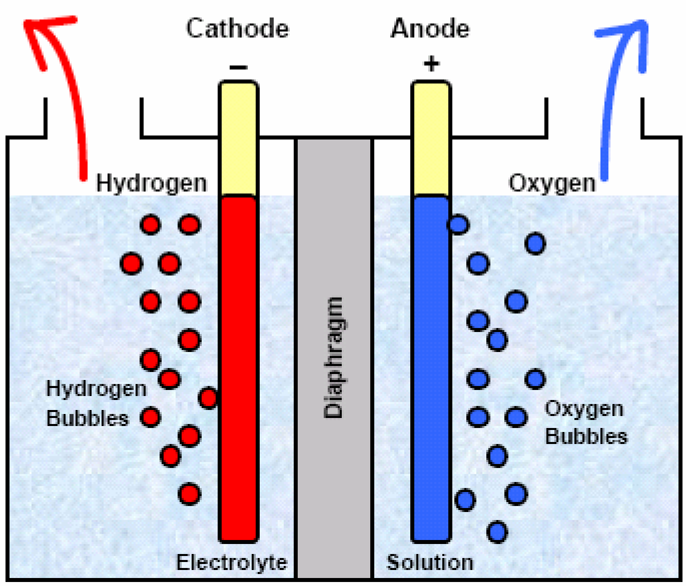
But how is the bond broken? We photodissociate the water, using energy from the sun to split it. The whole point of using sun energy is because it’s an environment-friendly and infinite source of energy. We can’t, however, just expose the water to sunlight, as the water would simply be boiled (that would be breaking its intermolecular bonds, which are the bonds that stick molecules together, not atoms themselves). We need to, somehow, turn the sunlight into electricity through some sort of solar cell, such as a solar panel.

The water splitting reaction looks like this:

$$2H_2O \rightarrow H_2 + 2O_2$$

In order to pass the electricity through the water, we need to prepare a solution with a good electricity conductor, because pure water does not conduct electricity as well as an ionized solution. Table salt, NaCl, is a very abundant, inexpensive and highly effective conductor. However, when the electric current passes through the water, chlorine ions (Cl-) turn into chlorine gas, which happens to be a highly toxic gas, used as the first chemical weapon. Essentially, if NaCl is used, we would be making hydrogen and chlorine gas, as opposed to hydrogen and oxygen. On the cathode, chlorine ions are oxidized and turned into chlorine gas. It reacts both with the copper, forming copper chloride (green solid that can be clearly seen in the solution) and NaOH, when reacting with the sodium ions that dissociated from the salt. For this reason, hydroxide solutions are more appropriate for this reaction. NaOH (sodium hydroxide) and KOH (potassium hydroxide) are some examples of good conductors for this specific reaction.

Below is a picture of the model and how a simple electrolysis cell looks like.



Standard Electrolysis

Despite copper being one of the best electricity conductors, copper is easily oxidized. When the water is split and we get oxygen on the positive side of the cell, it oxidizes due to the reaction:

$4Cu + O_2 \rightarrow 2Cu_2O$

Since copper(I) oxide (Cu_2O) is not a good conductor, the oxidation of copper will disturb the reaction and prevent electricity from being conducted. The optimal solution would be to use highly conductive metals that don't oxidize, such as platinum and gold. However, the cost of these metals is extremely high, with platinum costing around $50.000 a kilogram.

An easy way of doing this experiment in a small scale is to make a .1M solution of KOH, and use electricity for splitting the water. Since this is an extremely energy consuming process, batteries aren't the ideal source of energy to be used. When doing this experiment (and many other variations of it) in my fieldwork, I used wires connected to a solar panel, transforming the solar energy into electricity, as opposed to using photons themselves to break the bond.

However, we run into the oxidation problem again. An inexpensive and fairly simple way to deal with this problem is to use two pieces of solid nickel, have them be immersed in the solution with part of the pieces of nickel outside the solution. The wires are tied to the nickel. Since the wires won't have direct contact with the solution, they will not oxidize. The nickel in this case is acting as an electrolyte.

Another issue to be addressed is the voltage obtained by the solar panel. The optimal voltage to be used in this cell lies somewhere between 2.5V and 3V, ultimately being 4V. Based on what I observed in my experiments, solar panels will usually give you far more than that, varying from a range of 12V to 22V. Voltage regulators can be used to cut down the voltage, as well as resistors in series. The easiest way for cutting down the voltage in this case, though, is using a piece of opaque cardboard to block a portion of the solar panel. With the use of a voltmeter, the voltage can be measured, and the area of the panel to be covered by the cardboard can be determined.

Photolysis, however, does not use electricity to break down chemical compounds. It uses photons - energy charged particles that carry over light - to break down the bonds. However, exposing water to light (sunlight, optimally) will not split the molecule. Since not every photon is highly charged enough to be able to break the OH bond in water, the bonds that would be broken would be the intermolecular bonds - bonds that hold together different water molecules. Therefore, the water would not be splitted, but simply boiled.

In photosynthesis, plants utilize a similar method for splitting the water. Plants, however, have highly sophisticated photosystems that absorb photons of different wavelengths, and use an electron transport chain for splitting the water. Dr. Nocera from Sun Catalytix (group that researches reliable energy storage and fuels from renewable energy) and his group designed a procedure that replicates the functions of the plant for this matter using different materials in a simply engineered artificial leaf.

They use a wireless system for capturing energy, with silicon based semiconductors and earth-abundant catalysts. The whole idea of this research was to replicate the way plants split water, and also generate an environment friendly and economically viable way for splitting water. The materials and resources necessary for this system are abundant and inexpensive. Their whole project can be summarized as “an artificial leaf”, for it replicates the functions of a leaf.

Even though the idea is to replicate the functions of a plant to a certain extent, in this method completely different materials are used. As mentioned previously, of the main points of the artificial leaf method is to use earth abundant and inexpensive materials to carry on the whole reaction.

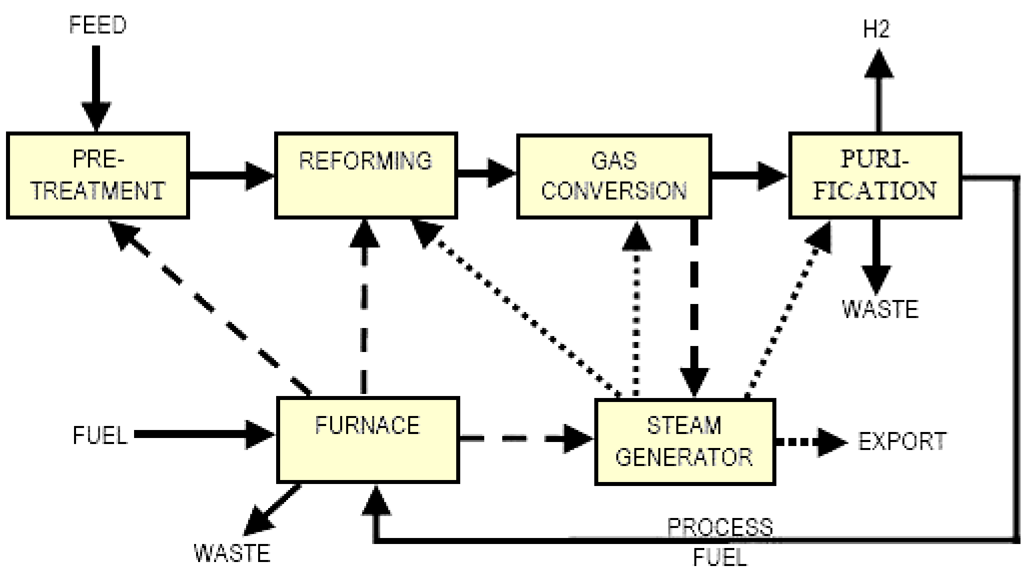
Photochemical cells have been successful at reasonable efficiencies. However, practical problems remain. A number of those cells rely heavily on expensive absorbing materials, such as (Al)GaAs and GaInP, and also fuel forming catalysts, $PtRuO_2$, IrO_2. Strongly acidic or basic media that are quite corrosive are extremely challenging to maintain in a large environment needed for light harvesting, an absolutely crucial part of the method used.

Therefore, the main focus nowadays of the water splitting research is on studying cheap ways of running a photochemical cell that works in a neutral pH environment, since corrosive media have been an issue. Dr. Nocera’s research, as mentioned before, has as its foundation the study and use of inexpensive and earth abundant materials for that matter.

Even though the cell is inexpensive, simply engineered and relatively cost effective, it isn't stable. After observing its performance, it has been established that there is a decline of 80% of its total efficiency. The cell was stable for 10 hours; afterwards there was a decline of 80% of its initial efficiency over 24 hours.

Steam reforming

The steam reforming process is illustrated in the picture below.



From coursework for Physics 240, Stanford, 2010

The most widely method used for obtaining hydrogen in a large scale is steam reforming. It uses water vapor, a natural gas such as methane and extremely high temperatures to obtain hydrogen. Below are the chemical reactions in the order in which they happen:

$$
\begin{array}{ll}
CH_4 + H_2O \leftrightarrow CO + 3H_2 & \Delta H_{295} = -206 \text{ kJ/mol} \\
CO + H_2O \leftrightarrow CO_2 + H_2 & \Delta H_{298} = -41 \text{ kJ/mol} \\
CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 & \Delta H_{298} = 165 \text{ kJ/mol}
\end{array}
$$

First, methane (CH_4) reacts with water vapor (H_2O) to form two products, CO and three molecules of H_2. Secondly, the CO product is reacted with water vapor in a second reaction, where we can obtain more hydrogen gas, and the byproduct will be CO_2. A second option is reacting one molecule of methane with three molecules of water. However, the byproduct of this reaction will be carbon dioxide, which is a toxic gas.

Doing the second reaction will, from some perspectives, defeat the purpose of this reaction. The idea of using H_2 as a fuel relies on the fact that it is a clean, environment friendly and cheap fuel. If the byproduct of the reaction necessary for obtaining the H_2 is CO_2, we might as well keep using the fuels we use today, such as gasoline and ethanol, since this process is extremely energy consuming and not easy to be performed.

Despite the problems, there is ongoing research on how to capture the CO_2 from the final reaction, and reuse it as an alternative energy method. However, even if a completely viable way of capturing the CO_2 is found, the production of hydrogen through steam reforming still wouldn't be viable. Even though the efficiency of steam reforming is far higher than the one of water splitting (by practically any method), its cost still needs to be lowered and its efficiency still needs to be increased in order for H_2 to be used as a viable fuel option.

Fieldwork and results

My fieldwork consisted of two weeks of water splitting experiments conducted in several different ways and with different materials and substances each time. The reason why I performed many variations of water splitting was to compare the effects of each, and how we can compare these micro-scale experiments to what happens in a macro-scale hydrogen production.

First, to have an insight and an idea of how the reaction looks like, and the speed in which it happens, I did the simplest variation of this experiment: I used copper wires, a simple beaker filled with a NaCl solution, and a solar panel. I opted for using a solar panel in the majority of my experiments since water splitting is a very energy consuming procedure, and solar panels are an infinite source of energy.

First experiment

Energy source: Solar panel

Voltage: Roughly constant at around 13V

Glassware: Beaker

Solution: NaCl

Electrolyte: N/A

Conductor: Copper wires

Observations/results: I tied copper wires to the solar panel wires, and directly immersed the copper wires into the solution. I started to see bubbles coming out (at first I thought they were H_2 and O_2). The positive wire (where, supposedly where the O_2 comes out) started to quickly oxidize. It turned to a green-ish color, and kept falling into a solution. It turned out that no O2 was being produced at all, but Cl_2. Chlorine ions were oxidized, and turned into chlorine gas. It reacted with copper (forming copper chloride, which explains the green color) and also reacted with sodium ions from the salt, forming NaOH, making the solution basic. As the wire oxidized, the less bubbles I could see, due to the less electricity being carried by the wires. A chlorine gas smell was very evident as well, a smell very similar to a swimming pool.

Second experiment

Energy source: Solar panel

Voltage: Roughly constant at around 13V

Glassware: Beaker

Solution: NaCl

Electrolyte: Graphite

Conductor: Copper wires

Observation/results: In my second experiment, I tried dealing with the oxidation issue. I decided to use graphite as my electrolyte, for carbon won't oxidize, and it conducts electricity fairly well. I sharpened two pencils at both ends; left a big piece of graphite exposed, and tied the copper wires to an end of each pencil. I immersed the pencils in water, and the results weren't very different from the first experiment, except for the fact that there was no oxidation. I left the pencils sitting there will the electric current passing through them for a weekend. After three days, there were still bubbles coming out. The chlorine gas smell was extremely strong, the graphite had dissolved a small amount (enough for the water to become grey and to make it harder for me to see the bubbles), and the pencils were now deformed.

The water level didn't change more than 1 centimeter, and it was mostly because of evaporation. This shows how slow the water splitting reaction occurs without a catalyst.

Since I was using an open container (beaker) to perform the reaction, I couldn't see how much H_2 was being produced. Since gas expands, I couldn't predict either. I decided to run my next experiment using a Hoffman Apparatus to see how much H_2 and O_2 were being produced.

Third experiment

Energy source: Solar panel

Voltage: Roughly constant at around 19V

Glassware: Hoffman apparatus

Solution: NaCl

Electrolyte: Silver sheet

Conductor: Copper wires

Observation/results: I filled the Hoffman Apparatus with a solution of NaCl. The day was sunny, therefore the solar panel was yielding more voltage, around 19V. As the reaction started, bubbles could be clearly seen coming out from the silver sheets, and the gas was being accumulated at the top of the apparatus, Cl_2 in one side and H_2 on the other side. The H_2 could be clearly seen, as it was being accumulated at the top of the apparatus. However, the Cl_2 could barely be seen. Because I used a NaCl solution, the Cl_2 disturbed the reaction again. It almost looked like there was no gas on the other side.

Fourth experiment

Energy source: Solar panel

Voltage: Roughly constant at around 19V

Glassware: Hoffman apparatus

Solution: .1M solution of KOH

Electrolyte: Silver sheet

Conductor: Copper wires

Observation/results: With the proper lab safety equipment, I prepared 300ml of a .1M solution of KOH. I used about 16.83 grams of KOH for 300ml of water. I poured the solution inside the apparatus, and repeated the steps in my third experiment. This time, however, I could clearly see the bubbles forming on both sides, as the chlorine isn't a problem anymore. The reaction still happens slowly.

Fifth experiment

Energy source: Two 1.5V AA batteries

Voltage: Roughly constant at around 3V

Glassware: Beaker

Solution: .1M solution of KOH

Electrolyte: Nickel rod

Conductor: Copper wires

Observation/results: I bought a solid nickel rod, cut it into two 3in pieces, and used them as electrolytes. I used the .1M KOH solution, immersed the two pieces of nickel into the solution (with part of it outside the solution) and wrapped the copper wires that were attached to the batteries to the ends of the pieces of nickel. Since the nickel served as the electrolyte, the wires didn't rust. Both pieces of nickel were covered in bubbles. This time I didn't use the solar panel as my source of energy because it is challenging to narrow down the voltage of something as inconsistent as a solar panel. The smallest voltage regulator I could find was a 5V regulator, and since 4V is the ultimate voltage for this experiment, it wouldn't work. Resistors in series wouldn't work either, because the voltage yielded by the panel is inconstant (might range from 12V to 19V in one day), therefore it would oscillate a lot if I used the resistors. Since my experiment wouldn't be in a macro-scale or a long term experiment, I used two 1.5V AA batteries, resulting in a total of 3V.

Sixth experiment

Energy source: Two 1.5V AA batteries

Voltage: Roughly constant at around 3V

Glassware: Hoffman Apparatus

Solution: .1M solution of KOH

Electrolyte: Nickel rod/silver sheets

Conductor: Copper wires

Observation/results: I decided to try to run the experiment with the nickel rods, but using the Hoffman apparatus. I placed the nickel rods on the top of the silver sheets, but the surface area contact was not big enough. There were almost no bubbles at all. In order for this to work, the nickel would have to be directly attached to the copper wires, having more surface area contact in order for the reaction to happen.

Since steam reforming requires extremely high temperatures, natural gas and many supplies to which I don't have access, I wasn't able to replicate any experiments related to hydrogen extraction from natural gases.

Use of hydrogen as a fuel in the real world

A potential use for hydrogen in the near future is its mass production and commercialization and a fuel. It is an environment friendly fuel, as it does not emit greenhouse gases when burned. It is also a renewable fuel. When hydrogen combusts and reacts with oxygen, the following reaction happens:

$2H_2 + O_2 \rightarrow 2H_2O$

The product of the oxygen and hydrogen combustion reaction is water. The water will go back to the environment, and will be reused in future water splitting methods to become a fuel once again. This makes this fuel clean, as the only product of the reaction is water, no greenhouse gases, and it also makes it renewable, as it can be reused.

However, as mentioned in the water splitting section, the big majority of the water splitting methods are extremely energy consuming, and it wouldn't be economically viable to hydrogen to be used in a large-scale production as a fuel.

Differently than gasoline, the hydrogen price is based on its mass as opposed to its volume. In order for it to be as cost effective as gasoline or other fuels commonly used nowadays, a kilogram of hydrogen should cost about $1.80. One kilogram of hydrogen is equivalent to one gallon of gasoline. However, in order to get 1kg of hydrogen, big amounts of energy need to be put in. As described earlier, the methods we have nowadays aren't stable enough to generate hydrogen for a long period of time constantly, or they are not cost effective, meaning the photochemical cost is way too high for the hydrogen fuel production to become economically viable.

Conclusion

Every day we are a step closer to finding the optimal water splitting method. Dr. Nocera's method is effective and inexpensive. However, it isn't stable if earth-abundant materials and substances are used, as the efficiency of the cell declines drastically. In a large-scale hydrogen production, steam reforming might be economically viable, but it isn't environment friendly, which is one of the main goals of this research.

Ongoing research is being made on both how to stabilize photochemical cells and the study of inexpensive stable catalysts, and also to capture and have a practical use for the CO_2 collected as the byproduct from the steam reforming final reaction.

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