

ET3034TUx - 6.3 - Solar Fuels

This week I shall discuss different ways on how to use solar energy in a less conventional way.

In past weeks, we have discussed how to convert light into electricity.

Also, in the previous blocks this week, we talked about conversion of solar energy into heat.

The last option is to convert solar energy into chemical energy, which allows us to directly create fuels.

But why is that so important?

Why would we want to create fuels instead of electricity or heat?

Since the sun does not always shine, solar energy is not constant.

There are two types of variations, the daily variations, meaning the difference between day and night, and the seasonal variations, because the sun's irradiation in the winter is not the same as in the summer.

But even if there is no sun, we expect our energy need to be always covered.

That is why we need some kind of storage, to be able to cover the electricity demand even when there is no sun.

Actually, the biggest problem in the current energy scenario is not the production of renewable energy, but its storage.

We know how to efficiently harvest the energy around us, but we don't have a reliable way to store it.

There are several forms of storing energy that we can use.

The graph here is called a Ragone plot.

Ragone plots show the amount of energy stored in a certain storage technology per kilogram of material with respect to the power provided by the technology per unit of mass.

The most used form of stored energy are fossil fuels.

As the graph shows, fossil fuels have high energy density properties, are stable and reliable.

But fossil fuels are depleting and their use is detrimental to our environment.

Hydrogen has an even better gravimetric energy density compared to fossil fuels, but it is a very light gas, so the volumetric energy density, i.e.

the energy per unit of volume, is much lower.

That is one of the reasons it has not been widely used until now.

However, if we compare batteries and hydrogen for the energy storage of a solar cell, batteries have a lower energy density and assume a much higher initial investment than hydrogen.

Also, hydrogen can effectively be produced from solar energy by utilizing electrochemistry.

This is why the concept of solar fuels is interesting and being discussed here.

Nature has been converting the energy from the sun into chemical energy for a long time by converting carbon dioxide and water into oxygen and sugars using sunlight.

That is what we call photosynthesis.

Now, we want to imitate this process with inorganic semiconductor materials.

These materials are able to split a water molecule into oxygen and hydrogen using the energy of sunlight.

That is why sometimes these technologies are referred to as artificial photosynthesis.

Let's now focus on the chemical cycle of hydrogen.

Water is split into hydrogen and oxygen by electrolysis.

Then, the hydrogen is combined with carbon dioxide in a water gas shift reaction to obtain carbon monoxide and hydrogen.

This gas mixture, known as synthesis gas, can be then refined in a Fischer-Tropsch reaction to finally obtain methane.

This conversion from hydrogen to methane is done because methane is easier to store and has less hazardous problems than hydrogen.

When the energy needs to be released, the methane can be burnt in a combustion reaction, which will also need oxygen and will give water and carbon dioxide as by-products.

This water is reused for the electrolysis and the carbon dioxide for the water gas shift reaction, thus closing the cycle.

Each reaction and each process of the cycle will have a certain efficiency, and the overall efficiency is the combination of all those efficiencies.

Now that we know why we want to produce hydrogen, let's see how we can do it with solar energy.

One of the best ways to produce hydrogen using solar energy is using a photoelectrode.

A photoelectrode is named as such because it uses light to produce an electrochemical reaction, in which water is split into oxygen and hydrogen.

In this process, the photons reach the surface of the photoelectrode, which is made of a photoactive semiconductor.

As in any other semiconductor, the photons with the same or higher energy than the semiconductor band gap energy create an electron-hole pair.

The electrons and holes will be separated by an electric field, and both will be used in the two half reactions involved in the overall water splitting process.

To create that electric field, this is coupled with a voltage source, for example a solar cell.

The solar cell will receive the transmitted light from the photoanode, creating another electron-hole pair and electric field that will bring the electrons to the photoanode and the holes to the photocathode with enough potential to drive the redox reaction in the electrolyte, splitting the water molecule into oxygen and hydrogen.

The reaction of water splitting is a reduction-oxidation reaction, or how they are commonly known, a redox reaction.

In redox reactions, the reaction happens due to the exchange of electrons between elements or molecules.

They can be divided in two half reactions: the oxidation or loss of electrons and the reduction or gain of electrons.

The oxidation happens in the anode and the reduction happens in the cathode.

In this case the reduction reaction is the formation of hydrogen with protons in the solution and electrons coming from the electrode, and the oxidation is the splitting of water giving oxygen molecules, protons to the solution and electrons to the anode.

Each half reaction has a potential associated, and the sum of the potential of each half reaction gives us the potential for the whole redox reaction.

But potentials are always defined with respect of a reference, a zero that we define.

For redox reactions, the zero is defined as the hydrogen half reaction.

So in the case of water splitting, the oxygen production reaction has a potential of 1.23V with respect to the hydrogen reaction, and therefore, the overall potential needed for the reaction to happen will be 1.23V.

Depending on the electronic properties of the semiconductor material it can either be treated as a donor or n-type semiconductor material, or as an acceptor or p-type semiconductor.

The band bending of the semiconductor can then go in two ways, depending on the semiconductor type.

If it is p-type, the material will attract more holes to the interface, and that will enhance the reduction half reaction, producing hydrogen in the photoelectrode or photocathode.

If the semiconductor is n-type, the opposite happens.

Electrons are moved to the interface by the internal electric field, and those electrons are involved in the oxidation half reaction, producing oxygen.

N-type semiconductor photoelectrodes are also called photoanodes.

As mentioned, in the photoelectrolysis, a photoactive semiconductor is used as an electrode.

This material has to fulfill several requirements.

First, it has to absorb the light that arrives to the surface.

Another important feature is an efficient charge carrier transport inside the material and separation into the two electrodes.

It has been estimated that material with an energy band gap close to 2.1 eV has the potential to split water, taking into account required overpotentials to drive the reaction.

In addition, the energy levels of the material have to be adequate to couple with the energy needed for the reaction.

This is what is called a favorable band edge position, meaning that the energy levels of the reactions have to be located somewhere in the energy band gap of the semiconductor.

To further enhance the reaction, a catalyst may be added to the semiconductor surface.

Finally, on the practical side, it is important that the material is photochemically stable and relatively cheap.

From these criteria, the main technical challenges to be addressed are the light absorption, the separation of charges and the catalysis of the reaction.

The absorption and catalysis problems can be tackled by carefully choosing the semiconductor material and its corresponding catalyst.

There are several materials that can be considered for solar water splitting.

Some of the most popular materials studied for this application are titanium dioxide (TiO₂), tungsten oxide (WO₃), bismuth vanadate (BiVO₄), iron oxide (Fe₂O₃) or silicon carbide (SiC).

These last three materials are the ones with a more promising future judging by their potential solar-to-hydrogen efficiency, as shown in the graph.

When looking at the optimum band gap, iron oxide and silicon carbide are the best choice for the optimum absorption of light, since they have band gap energies closest to the optimal 2.1 eV.

But if considering the other factors like band position or stability, materials like bismuth vanadate may also be a viable option.

The rest of the materials are not considered, such as titanium dioxide or tungsten oxide, because they have lower maximum theoretical efficiencies due to their large band gap energies.

There are two main factors on which the efficiency of the overall water splitting device depends: The catalytic efficiency and the separation efficiency of the photoelectrode.

The catalytic efficiency can be improved by placing a catalyst in the surface of the semiconductor.

For example, for a bismuth vanadate photoanode the inclusion of a cobalt phosphate catalyst on the surface will ease the oxidation reaction and the water splitting efficiency will be higher. The separation efficiency can be improved by introducing an electric field inside the material.

One way to do this is to introduce gradient doping, from no doping at the surface to 1% doping close to the back of the electrode.

That way we create a depletion region in between the semiconductor and the electrolyte that will more easily move the electrons from the electrolyte into the semiconductor.

The combination of both effects can highly improve the efficiency of the overall device.

For the photoelectrochemical water splitting process, at least the potential difference of 1.23 V must be given to directly split water.

Then an overpotential has to be applied to compensate for the extra losses in the electrodes and the activation energy needed for the reaction.

This value will depend on the materials and electrolyte used, but it is usually around 0.8 V.

Both potentials added will result in the total potential difference needed to drive the redox reaction.

This voltage will be partly covered by the potential difference created within the photoelectrode when light shines on it.

But that only compensates for around 0.6 V of the needed voltage, depending on the material used, which is not enough.

That is why these photoelectrodes are often combined with solar cells that give the extra potential needed for the reaction to happen.

The combination of a photoelectrode and a solar cell forms a photoelectrochemical device.

And if you are asking yourself how such a device will work, I will explain it right now.

The photoelectrode, let's say a photoanode, is connected in series to a solar cell.

So the photoanode of the example will be connected to the positive part of the solar cell and then the negative part of the solar cell will be connected through an external circuit to another electrode, which may or may not be photoactive.

The circuit will be closed by the electrolyte.

Since both devices are in series, the same current should go through both parts the same way we explained in tandem solar cells.

In this device, the light is also utilized more.

When the light strikes the photoelectrode surface, the light corresponding to the band gap of the photoelectrode will be absorbed there.

The rest of the light that has not been absorbed or reflected, called the transmitted spectrum, goes to the solar cell where it can be absorbed to produce the extra potential difference to separate charges and drive the reaction.

The solar cell must be especially designed to function with the transmitted spectrum, since the light will have a different spectrum and intensity than the standard solar spectrum AM1.5.

The photoelectrode, as any other semiconductor device, has its own characteristic J-V curve.

When a solar cell and a photoelectrode are combined, the conditions at which they will work can be calculated by studying their J-V curve characteristics.

I already discussed the J-V curve of a solar cell in previous lectures which looks like the red curve here.

Now, if we include the J-V curve of the photoelectrode, a photoanode in this case, represented by the black line, we can get the current and voltage at which the device will work, the operational point.

Since both elements are connected in series, the current of both the solar cell and the photoelectrode must be the same.

So the operational point will be where both J-V curves cross.

The solar-to-hydrogen efficiency of the device is related to the amount of hydrogen that is produced, which is directly calculated by the current density measured at the operating point.

The idea is that current is basically charges moving per unit of time, and we assume that all charges produced are involved in the reaction of hydrogen production.

Mathematically, the overall solar-to-hydrogen conversion efficiency, is described as the operational current density J_{photo} multiplied by 1.23 V, the redox potential, and divided by the irradiance arriving to the surface of the photoelectrode, P_0 .

The higher the operational current, the more hydrogen is produced and the higher the efficiency of the device.

That is why researchers are focusing in improving the current density that this device can give.

We talked about gradient doping and the use of water oxidation catalysts.

There are other improvements that can be done to increase the performance of such a device, such as the design of the materials and thickness of a silicon thin-film tandem cell or the texturing of the photoanode for better light trapping.

Applying all those concepts, we here at the Delft University of Technology have developed a device made with a bismuth vanadate photoanode combined with a double junction amorphous silicon solar cell and a platinum cathode.

This device has achieved a solar-to-hydrogen efficiency of 4.9%, which is actually the highest efficiency reported for such devices based on a metal oxide photoanode.

This week we have discussed the third generation technologies, solar thermal and solar fuel approaches.

Next week, we will start building and designing a PV system.

I will introduce you to all important components in the PV system.

See you next week!