

23

Solar Fuels

In this chapter we discuss how to store solar energy in the form of chemical energy in so-called *solar fuels*. As we have seen in previous chapters, we are able to convert solar energy to electricity with efficiencies of up to 44%. Also, we are able to convert solar energy easily in heat, which we can use for preparing warm water, heating and even cooling.

The biggest obstacle towards a economy that is driven by renewable energy is not the generation of sustainable energy sources but the storage the renewable energy. As we have seen in Chapter 19, storing electricity with batteries is very difficult. While day-night storage that makes solar electricity generated during daytime available in the night is easily done, seasonal storage that allows to store electricity generated in the summer until winter would require very large battery systems that usually are not feasible. This problem becomes more severe in regions that are far away from the Equator such that the differences in solar irradiance between summer and winter are significant. The same also is true for solar heat that was discussed in Chapter 22: while a hot water storage tank with a volume of several hundreds of litres is sufficient as day-night storage, seasonal storage that would allow to use solar-heated water throughout the year would require storage tanks with a volume of tens of thousands litres. This tank also would need to be heavily isolated. If we manage to store solar energy as chemical energy, we do not have this problem as chemicals can be easily stored.

Fig. 23.1 shows the Ragone chart in that we already analysed in Section 19.3. The chart shows the amount of energy per mass stored in a certain storage technology versus the specific power provided by the technology. As we know, by far the most used form of stored energy are fossil fuels. As we can see from the graph, fossil fuels have high energy density properties, are stable and reliable. But, fossil fuels are depleting and their use is detrimental to the environment. Hydrogen (H_2) has an even better gravimetric energy density than fossil fuels, but it is a very light gas. Hence, the volumetric energy density, *i.e.* the energy per unit volume, is much lower. This is one of the reasons it has not been widely used until now. When we compare batteries and hydrogen as energy storage for solar electricity, we see that batteries have a lower energy density. Further, they require a much higher initial investment than hydrogen. Hence, it seems an interesting option to use hydrogen as a storage material, *i.e.* as a solar fuel.

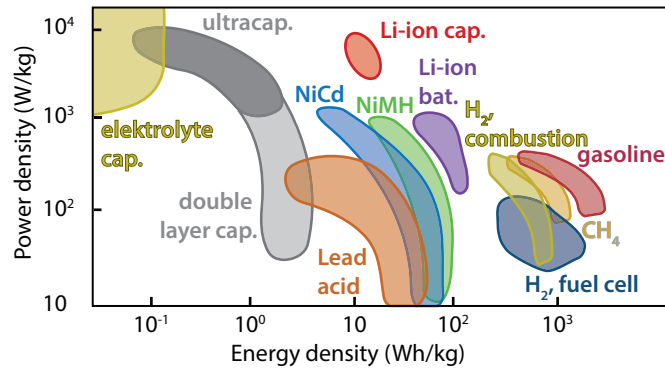
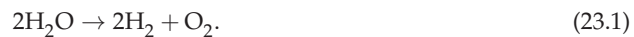


Figure 23.1: Ragone chart of different energy storage methods. Capacitors indicated with “cap”.

In this chapter we discuss how to produce hydrogen using solar energy by utilising electrochemistry. In nature, *photosynthesis* takes place, where sunlight is used to convert carbon dioxide and water into oxygen and sugars, which can be seen as 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. Here, we try to mimic nature with inorganic semiconductor materials that are able to split a water molecule into oxygen and hydrogen using the energy of sunlight. This process sometimes is referred to as *artificial photosynthesis*.

For storing solar energy as chemical energy in the form of hydrogen, *water splitting* can be used,



The energy required for this reaction is given by the *Gibbs free energy* and it has a value of $G = 237.2$ kJ/mol. In *solar water splitting* this energy is provided by the Sun.

Another product that seems very promising for energy storage is *methane* (CH_4), as it is easier to store and has less hazardous problems than H_2 . It can be produced from hydrogen and carbon dioxide (CO_2) with the *Fischer-Tropsch process*. In this process, first the hydrogen is combined with carbon dioxide in a *water-gas shift reaction* to obtain carbon monoxide and water in the form of steam,



This gas mixture, known as *synthesis gas*, can be then refined to finally obtain methane,



When the stored energy is required, the methane can be burned in a combustion reaction,



that will give water and carbon dioxide as byproducts. The water can be reused for the electrolysis and the carbon dioxide can be used for the water gas shift reaction, hence, the cycle is closed. Each reaction in the cycle has a certain efficiency; the overall efficiency can be obtained by combining all those efficiencies.

Many different methods can be used for water splitting. In this chapter we will discuss two methods: *electrolysis of water* and *photoelectrochemical water splitting* (PEC).

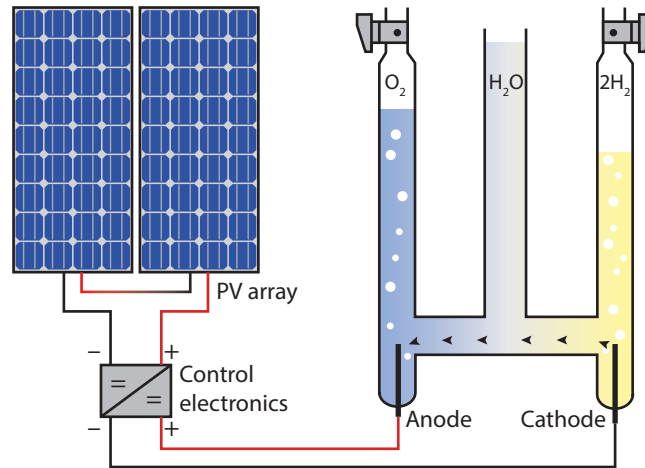


Figure 23.2: Illustrating a lab-scale Hofmann voltameter that is used to split water. In the sketch the voltameter is connected to a PV system via some control electronics.

23.1 Electrolysis of water

Figure 23.2 shows a typical lab-scale setup for the hydrolysis of water. It is called a *Hofmann voltameter* after the German chemist August Wilhelm von Hofmann (1818-1892). It contains of three upright cylinders that are joined at the bottom. While electrodes are placed in the left and the right cylinder, the central cylinder is used to refill the device with water. For starting the electrolysis, a voltage has to be applied between the two electrodes.

Water splitting is a *reduction-oxidation* reaction, which is commonly abbreviated as *redox reaction*. In such redox reactions, the reaction happens due to the exchange of electrons between atoms or molecules. They can be divided in two half reactions, the *oxidation* and the *reduction*. For water splitting these half reactions look as follows: During the oxidation, which happens at the *anode*, water is split giving oxygen and protons to the solutions and electrons to the anode,



In the reduction, electrons originating from the *cathode* react with the protons to hydrogen,



The total reaction therefore can be written as



Each half reaction has an associated potential and the sum of the potentials of each half reaction is the potential for the whole redox reaction. Potentials always are defined with respect to a reference, *i.e.* a zero point. For redox reactions, the zero is defined as the hydrogen half reaction that happens at the cathode. For calculating the potential at the anode, *ie* of the oxygen production reaction, we can apply the equation

$$V^0 = \frac{G}{nF} \quad (23.8)$$

where G is the Gibbs free energy already mentioned above, n is the number of electrons transferred between the anode and the cathode for the production of one H_2 molecule, and $F = 96\,485\text{ C/mol}$ is the *Faraday constant* that tells us the amount of charge per mole of electrons. Using $G = 237.2\text{ kJ/mol}$ and $n = 2$, as two electrons are transferred per H_2 molecule, we find $V^0 = 1.23\text{ V}$.

In reality, an applied voltage of 1.23 V is not enough to drive the redox reaction because of some voltage losses. These voltage losses are mainly because of the activation energy at the electrodes as well as Ohmic losses in the cables, electrodes and also in the solution. For increasing the conductivity of the water, a base or an acid can be added. For the classic Hofmann voltameter, a small amount of sulphuric acid (H_2SO_4) is used.

The potential difference between V_0 and the potential used in the real device is called *overpotential* ΔV . The overpotential due to the activation energy required at the electrodes is strongly related to the electrode material and the gas that is produced at that electrode. For hydrogen production at the cathode, *platinized (black) platinum* is one of the best materials with an overpotential of -0.07 V . For the oxygen production at the anode, *nickel* with an overpotential of $+0.56\text{ V}$ is very well suited. Combining these two voltages and the overpotentials we can understand that the typical overpotential is usually around 0.8 V .

It is important to realise that all the energy consumed by the hydrolysis process related to the overpotential is lost and will lead to heating of the hydrolysis device. Only a fraction

$$\eta_{WS} = \frac{V^0}{V^0 + \Delta V} \quad (23.9)$$

of the supplied energy is actually stored in hydrogen. It is clear that it is a very important task for science and industry to reduce the required overpotential. Further, the current requirement for platinum electrodes makes hydrolysis not feasible from an economic point of view.

For an overpotential of 0.8 V , we would get an efficiency of around 60% . If we would use a good PV system with an overall efficiency of $\eta_{PV} = 18\%$ we would have a total maximal *solar-to-hydrogen efficiency* of

$$\eta_{STH} = \eta_{PV}\eta_{WS} = 10.9\%. \quad (23.10)$$

23.2 Photoelectrochemical (PEC) water splitting

Hydrogen can also be produced utilising solar energy by using a *photoelectrode*, which 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, photons with an energy equal or larger than the semiconductor band gap energy will 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 generate the required electrical field, we need a voltage source, for example a solar cell. The photoelectrode can be either an anode or a cathode.

If the solar-splitting device is made of a solar cell that is placed behind the photoanode, the solar cell will receive the light transmitted through the photoanode. This light creates another electron-hole pair and electric field that brings the electrons to the photoanode and the holes to the photocathode with enough potential to drive the redox reaction in the electrolyte. As a result, the water molecule is split into oxygen and hydrogen.

When the photoelectrode is made from an *n*-type semiconductor it acts as electron donor; if it is *p*-type it acts as electron acceptor. As an acceptor, the material will attract more holes to the interface, which will enhance the reduction half reaction. Hence it acts as the photocathode and

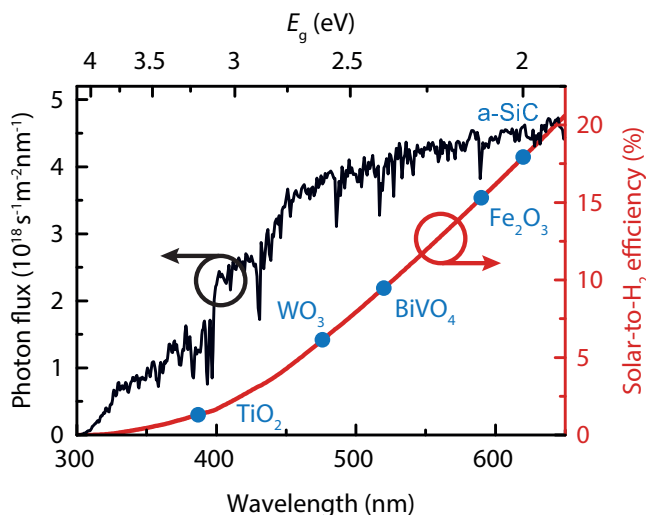


Figure 23.3: The solar-to-hydrogen efficiency and bandgap of different potential photocathode materials. Also the photon flux is shown.

produces hydrogen. If the semiconductor is *n*-type, it acts as the photoanode. Electrons are moved to the interface by the internal electric field, and those electrons are involved in the oxidation half reaction, such that oxygen is produced.

The semiconductor material has to fulfil several requirements:

1. It has to absorb light incident on its surface.
2. Charge carrier transport inside the material and separation into the two electrodes must be efficient.
3. A bandgap of 1.23 eV is not enough to drive the reaction because of the overpotential already discussed above. It has been estimated that materials with an energy band gap close to 2.1 eV have the potential to split water.
4. The energy levels of the material have to be adequate to couple with the energy needed for the reaction. In particular, the energy levels of the reactions have to be located in the energy band gap of the semiconductor, which is called the favourable position. To further enhance the reaction, a catalyst may be added to the semiconductor surface.
5. On the practical side, it is important that the used materials are photochemically stable and relatively cheap. From these criteria we can conclude that the main technical challenges to be addressed are 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. Several materials can be considered for solar water splitting. Some of the most popular materials studied for this application are titanium dioxide (TiO_2), tungsten oxide (WO_3), bismuth vanadate (BiVO_4), hematite (Fe_2O_3) or amorphous silicon carbide (a-SiC). As shown in Fig. 23.3, BiVO_4 , Fe_2O_3 , and a-SiC have the most promising potential solar-to-hydrogen efficiency. Hematite and silicon carbide are the best choice for the optimal absorption of light, since they have band gap energies closest to the optimal bandgap of 2.1 eV. However, if also other factors such as the band position or stability are considered, materials like bismuth

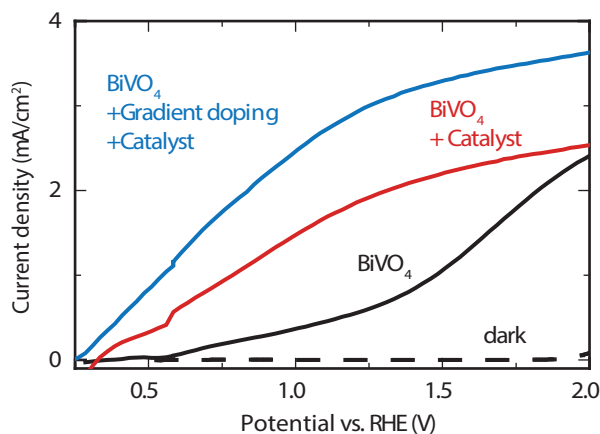


Figure 23.4: The effect on using a catalyst and gradient doping on the performance of a BiVO_4 photoanode [192].

vanadate may also be a viable option. Because of their large bandgap energies, the other materials are not considered.

The overall efficiency of water splitting depends on the catalytic efficiency and the separation efficiency of the photoelectrode. The *catalytic efficiency* can be improved by placing a catalyst on the semiconductor surface. For example, for a BiVO_4 photoanode the inclusion of a cobalt phosphate $[\text{Co}_3(\text{PO}_4)_2]$ catalyst on the surface will ease the oxidation reaction and hence increase the water splitting efficiency. The *separation efficiency* can be improved by introducing an electric field inside the material. One way to do this is to introduce gradient doping, starting from no doping at the surface to 1% doping close to the back of the electrode. With gradient doping a depletion region is created in between the semiconductor and the electrolyte. As a result, electrons will move more easily from the electrolyte into the semiconductor. Combining both effects can highly improve the efficiency of the overall device. Both the effects of the catalyst and the gradient doping are shown in Fig. 23.4, where the current density of the illuminated photoanode is shown in dependence of the applied voltage with respect to the *reversible hydrogen electrode* (RHE). The RHE is a special electrode with the property that the measured potential does not change when the pH value of the solution is changed.

As we already mentioned above, for the photoelectrochemical (PEC) water splitting process, a potential difference of at least 1.23 V plus the overpotential ΔV must be present. The value of ΔV will depend on the materials and electrolyte used, but it is usually around 0.8V. Both potentials added will result in the total potential difference required to drive the redox reaction. This voltage will be partially covered by the potential difference created within the photoelectrode when light shines on it. However, depending on the material, the PEC only creates 0.6 V of the required voltage. For the extra potential that is required to allow water splitting, the photoelectrode can be combined with solar cells that provide the extra potential needed for the reaction to happen. The combination of a photoelectrode and a solar cell forms a photoelectrochemical device.

In Fig. 23.5 (a) such a PEC device is sketched. The photoelectrode (in this case a photoanode) is connected to a solar cell in series. The photoanode is connected to the positive contact of the solar cell. The negative contact of the solar cell is connected to another electrode via an external circuit. This counter electrode may or may not be photoactive. The electric circuit is closed by the electrolyte. The band diagram of this device is shown in Fig. 23.5 (b).

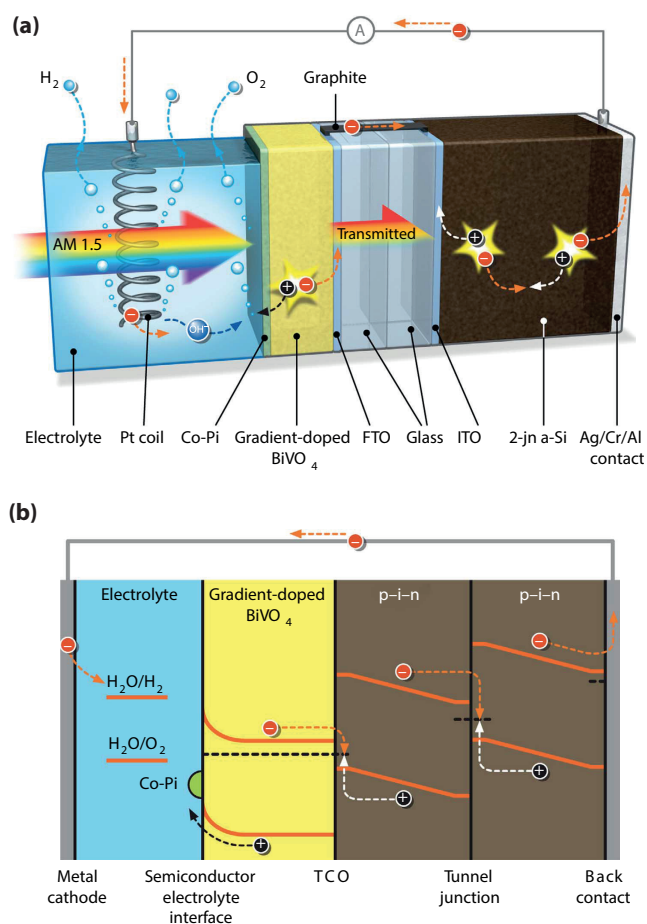


Figure 23.5: (a) Illustrating a photoelectrochemical (PEC) device consisting of a BiVO_4 photoanode and a tandem a-Si:H/a-Si:H solar cell. (b) The band diagram of this PEC device (Reprinted by permission from Macmillan Publishers Ltd: F. F. Abdi, L. Han, A. H. M. Smets, M. Zeman, B. Dam, and R. van de Krol, *Nature Communications*, vol. 4, 2195, copyright (2013)) [192].

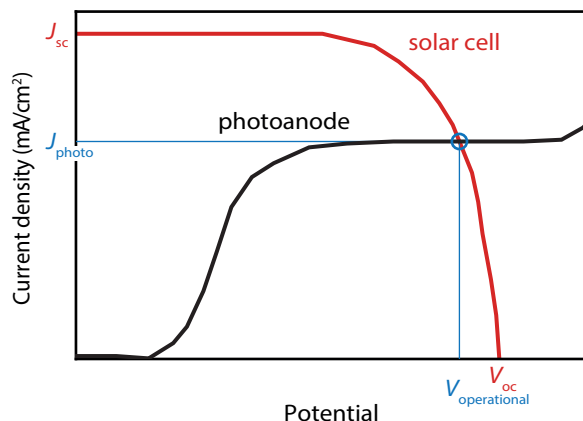


Figure 23.6: The J - V characteristics of the photoelectrode and the solar cell. The operating point is at the crossing of the two.

Since the photoelectrode and the solar cell are connected in series, the same current will go through both the devices, similar as for multi-junction solar cells. In this device, the light is utilised better than it would be in the solar cell alone. In the photoelectrode, the photons with energies exceeding that of the photoelectrode bandgap will be absorbed. The fraction of the light that has not been absorbed or reflected, called the *transmitted spectrum*, reaches the solar cell where it can be absorbed to generate the extra potential difference required for water splitting. The solar cell must be optimised for the transmitted spectrum, which is different from the standard AM1.5 spectrum that is usually used for solar cell optimisation.

As any semiconductor device, the photoelectrode 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 estimated by studying their J - V curve characteristics. Figure 23.6 shows the J - V curves of the solar cell and of the photoanode in this case. Since both elements are connected in series, the current of both the solar cell and the photoelectrode must be the same. Hence, the operational point will be where both J - V curves cross.

The *solar-to-hydrogen efficiency* η_{STH} is directly calculated from the current density measured at the operating point, which we can understand by realising that current is the flow of electric charge per time. When we assume that all generated charges produced are involved in the production of hydrogen, the overall solar-to-hydrogen conversion efficiency, is described by

$$\eta_{\text{STH}} = \frac{J_{\text{ph}} \times 1.23 \text{ V}}{P_{\text{in}}}, \quad (23.11)$$

where J_{ph} is the operational current density, P_{in} is the irradiance arriving at the PEC device, usually it will be 1000 W/m^2 from the AM 1.5 spectrum.

The only free variable in Eq. (23.11) is the current density: the higher the operational current, the more hydrogen is produced and the higher the device efficiency. The major focus of current academic research therefore is to improve the current density. Besides utilising gradient doping water-oxidation catalysts also other improvements can be done to increase the performance of PEC devices. These are optimising the materials and layer thicknesses in the used solar cell and texturing of the photoanode for better light management.