They work best under stress: microalgae as hydrogen factories

Home-grown hydrogen

In the search for alternative, environment-friendly sources of energy, microalgae are highly promising. They can produce hydrogen, which generates electricity in the fuel cell. In the EU project "Solar H", researchers are trying to optimize the algae system. The goal is an algae fermenter for home use.

Hydrogen is a highly promising candidate among future energy sources. The H_2 molecule with its simple structure has a high energy content and can be stored relatively easily. In a fuel cell, hydrogen combines with oxygen in the air to form pure water. Electricity is generated in the process, which can be put to

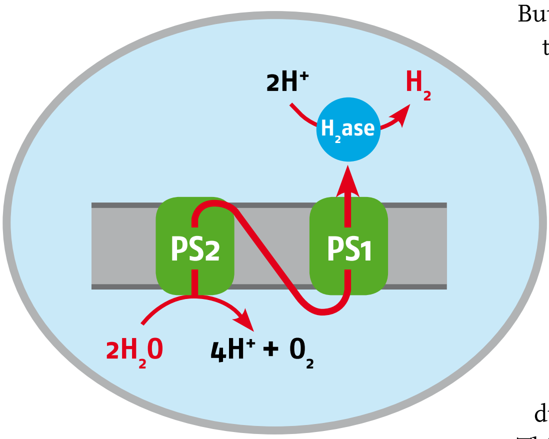


Fig. 2: Under stress conditions, hydrogen is produced in the algae as a waste product.

any use. This already works on a small scale, in cars for example.

So far so good, but where is the necessary hydrogen going to come from? At the moment it is generated by the cleavage of water using electricity produced from fossil fuels. Such fuel reserves are limited and emit CO_2 in the combustion process – so nothing has been gained. But for the future, biologists have discovered a small helper: the type of green algae called *Chlamydomonas reinhardtii*.

The microscopically small, single-cell plants which can also be found in garden ponds, convert light energy to chemical energy (sugar) by means of photosynthesis. This mainly involves two enzyme systems: photo system 2 (PS2) cleaves water, photo system 1 (PS1) uses light to transport the electrons required to convert CO_2 into sugar. This on its own of course would not make the algae particularly interesting: all green plants are able to perform photosynthesis. But *Chlamydomonas reinhardtii* has another ace up its sleeve: the ability to produce pure hydrogen with a certain enzyme (hydrogenase) at a rate of up to 5,000 H_2 molecules per second, practically as a waste product of photosynthesis (Fig. 2).

But there's a snag: if the algae are healthy, they do not form hydrogenase, and thus produce no hydrogen. They have to be put on a diet, withholding an important nutrient such as sulphur which impedes growth, before they form hydrogen to get rid of the surplus energy from the photosynthesis process. It is only under these actually unfavourable conditions that the algae expire more oxygen than they produce themselves by photosynthesis.

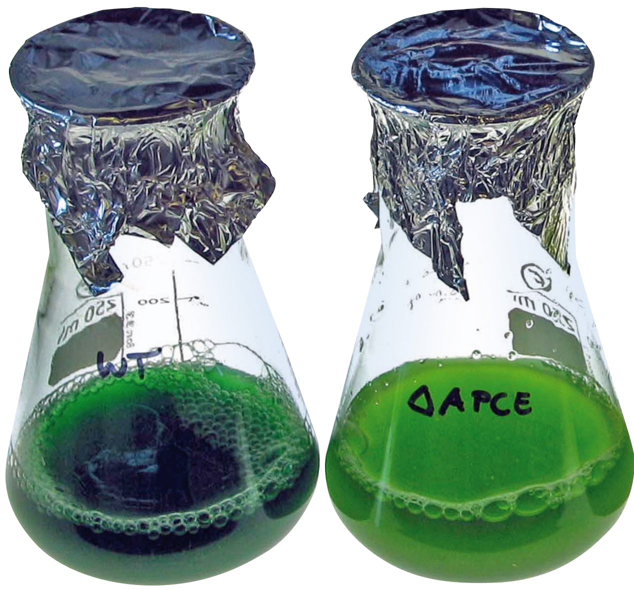
This in turn is the prerequisite for successful hydrogenase: contact with oxygen destroys the enzyme. But under these diet conditions, the algae only produce a fraction of their maximum possible quantity of H_2.

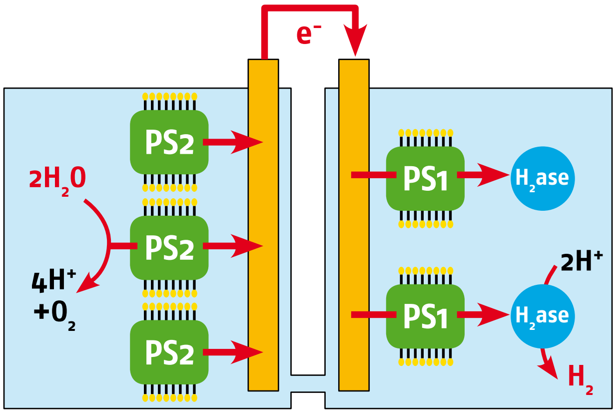
A corresponding algae reactor does function in a self-contained system under a strict diet, but this is no good for household use. Admittedly, at around five to ten percent, the efficiency of the algae is about the same as generating hydrogen using electricity from solar cells. But the deep green algae need light, so they can only be kept in vessels that are a maximum of 20 centimetres deep. It takes about 50 cubic metres of algae culture to supply a 3-man household with electricity from a fuel cell: this would need an area of about 250 square metres. And so the system has to be fine-tuned. Researchers

Researchers use algae components to make a biobattery

working on the EU project "Solar-H" (see Info) coordinated by Prof. Dr. Thomas Happe at the Chair of Professor Dr. Matthias Rögner are taking two different paths on the road to making efficient use of the ingenious principle.

On the one hand, they take the "components" of this and other types of algae and turn them into a semi-artificial system or, in simpler terms, a biobattery (Fig. 3). "The advantage of this is that it can be used to combine the individual parts of different organisms," Prof. Rögner explains. The system consists of two separate chambers. In the first, PS2 is fixed to a gold electrode and cleaves water into hydrogen and oxygen, thus releasing electrons: Bochum's biobattery has only one single layer





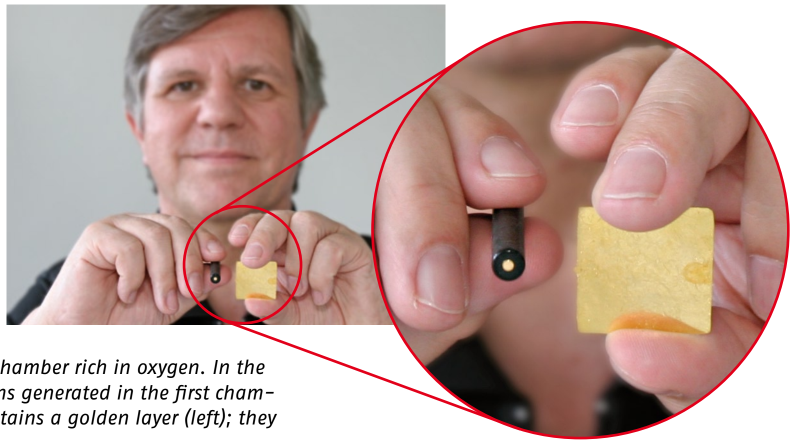


Fig. 3: How the biobattery works (fig. left). Water is cleaved in the left chamber rich in oxygen. In the right chamber, hydrogen is produced using the energy from the electrons generated in the first chamber. The electrodes of the biobattery are tiny (fig. right) – their core contains a golden layer (left); they could be enlarged for later use (right).

of PS2 on the electrode, but it cleaves approx. 1,000 times more water than previously described in publications by other researchers. While oxygen, which is fatal to the hydrogenase process, remains in this first chamber, the electrons pass through a wire into the second chamber. Here PS1 and the hydrogenase are again fixed to a gold surface. Here two hydrogen ions (protons) from the cleaved water are joined together with two electrons to form one molecule of pure hydrogen (Fig. 3).
The researchers are using this system above all for experimental purposes. Here they can integrate changed enzymes and test the efficiency of the overall system without having to take account of the complicated procedures taking place in a living organism. They have already managed to improve electron transfer by PS2 in the first chamber by not applying the enzyme directly to the electrode but by placing a polymer layer between the enzyme and the electrode. This layer contains “electron traps” for even better transfer (Fig. 4).
In the next step, the researchers will test another hydrogenase. Prof. Dr. Bärbel Friedrich from the Humboldt University Berlin has discovered a hydrogenase which is not susceptible to oxygen. But it has one big problem: it only produces one hundredth of the quantity of hydrogen produced in the same time by the oxygen-sensitive “turbo hydrogenase” of the green algae. But it is being used in the biobattery for test purposes. One variation of the hydrogenase is even directly connected to the PS1 so that electrons can pass directly between the two enzymes. Here again researchers hope for an improvement in efficiency. “The biobattery lets us try out various components before putting them back in natural systems such as the cyanobacteria (blue-green algae)”, Prof. Rögner summarizes. The biobattery cannot compete with the crucial advantages of living cells – the capacity for autonomous reproduction, which makes them more durable and less expensive than the semi-artificial system. Though it could play an interesting role as a sensor. Hydrogenase namely also works in reverse and can split hydrogen molecules into two protons, releasing two electrons. In fuel-cell cars for example, this could be used to detect leaks in the tank which are dangerous because of hydrogen's explosive risk.
The other path being taken by researchers is to improve the natural system, with researchers adjusting all the possible configurations. For example, the green algae hydrogenase can also be used in blue-green algae, which are single-cell organisms and thus simpler than the eukarotic green algae which have a nucleus. Genetic modification to the blue-green algae to make their light trapping antennae smaller gives them a lighter colour (Fig. 1). This has the advantage that they let more light through to the other algae further down in the fermenter. Although this makes the light entrapment of the individual cell less efficient, “the amount of light supplied by the sun is as a rule anyway too great rather than too small,” explains Pro. Rögner. Too much light even destroys the PS2, which heats up and expires under the excessive demands.
So it is important for the well-metered light to be distributed evenly. To achieve this, the biologists have developed a new kind of fermenter which is flat instead of round as in the past, and only five centimetres in diameter. The fermenter has been developed by Rögner's team toge-

Genetically modified algae are a paler green and let more light through

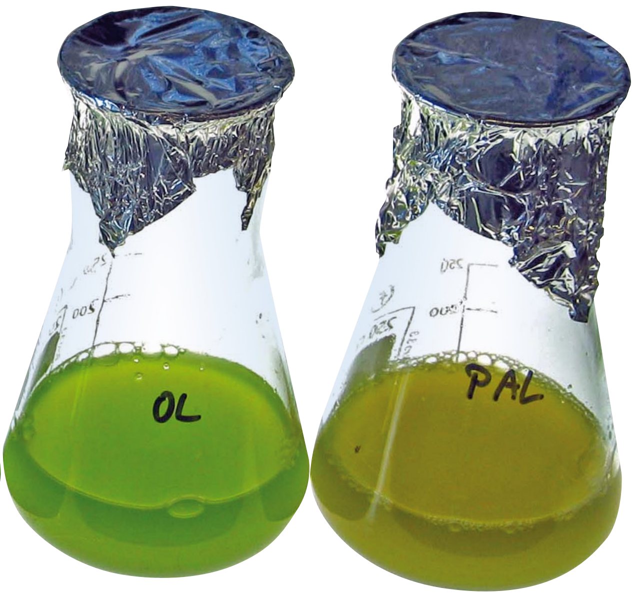


Fig. 1: Bottles with algae cultures. Mutants have a paler colour and thus let more light through to lower layers of algae.

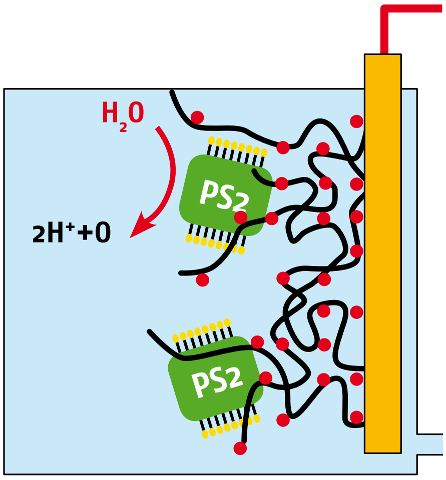


Fig. 4: The flat bed fermenter contains five litres of algae culture. In contrast to pillar-shaped fermenters, it offers a greater surface area and thus a more even distribution of light.

ther with a company in Hattingen (Fig. 5). It consists of industrially manufactured parts and is thus available at a much lower price than the previous laboratory version, consisting of a round column at more than head-height with countless measuring and calibration devices. "We won't need all these technical devices once we know what we have to do", says Rögner. As the cleaning of the new fermenter is chemical instead of using hot water vapour in the autoclave, the material also does not have to be so extremely heat-resistant. Plexiglas will do. The new fermenter currently costs less than ten percent of the price of a laboratory fermenter, and is still undergoing further optimization. "Once a few hundred of these devices have been sold, the price will sink even further", says Rögner confidently.

To make it even easier for the blue-green algae, the researchers have set out to find their favourite light wave: and round it in the red range. Ideally, blue-green algae use the light of red LEDs – unfortunately not those on sale in huge quantities at low prices, but those whose wavelength is further in the red range (Fig. 5). "Even so, it is still worth using these LEDs at what is currently ten times the price, because even if this only makes the hydrogen production two to three times more efficient, this makes a considerable difference", says Rögner.

His staff are also looking intensively at the inner workings of the microalgae to find possible approaches for further improvements. Proteome analysis – investigating all proteins present in the cell at a certain point in time under stipulated conditions – has already revealed that there are PS2 copies with differing compositions which are more or less light resistant and have different levels of efficiency in transferring electrons. Other cell reactions to different kinds of stress could also be interesting. But the prime aim is to make green algae hydrogenase unsusceptible to oxygen. This would permit operation of the green hydrogen factory not only under normal pressure and temperature conditions, but also in the air.

Improvement possibilities in the inner workings of microalgae

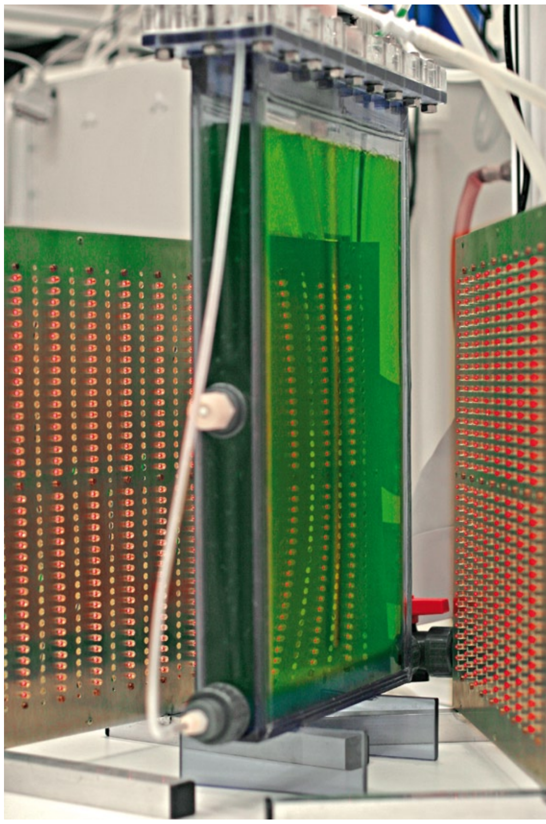


Fig.5: Cyanobacteria simply love the red LEDs with a wavelength of 720 nanometres, making optimum use of the light energy.

But one thing is quite sure: microalgae are good energy suppliers, even regardless of their role as a hydrogen producer. Their calorific value is between that of lignite and coal, they grow ten times faster than reed with their mass doubling every ten to twelve hours. But algae would not be algae if there wasn't a catch: at the moment it is still too cost-intensive to liberate the biomass from water.

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Solar-H combines molecular genetics and bio-mimetic chemistry

The project with the official title "Linking molecular genetics and bio-mimetic chemistry – a multidisciplinary approach to achieve renewable hydrogen production" is being coordinated by the University of Uppsala (Prof. Dr. Stenbjörn Styring, Sweden). Together with the Ruhr-Universität Bochum and the Max-Planck Institut für bioanorganische Chemie (Max Planck Institute for Bioinorganic Chemistry, Mülheim) in Germany, partners from France (Centre d'Etudes Atomique, Université Paris-Sud), Hungary (Biological Research Centre Szeged), Switzerland (Geneva University) and the Netherlands (Wageningen University) are also involved. The project is being funded initially for three years with €1.8 million. At the Ruhr-Universität Bochum, the activities are embedded in several other projects being funded by the Bundesforschungsministerium (BMBF – Federal Ministry of Research) and the Deutsche Forschungsgemeinschaft (DFG – German Research Foundation).

▶ Information on the internet: http://www.cordis.lu/nest, http://www.rub.de/bioh2/