Hydrogen~ fuel of the future?

Bubbles of hydrogen. They were produced from sunlight using apparatus developed at the CSIRO Division of Energy Chemistry.

Today's space vehicles propel themselves into orbit using the energy of hydrogen. Because of expected shortages in petroleum by early next century, cars of the future may also be running on that remarkable fuel.

The beauty of hydrogen is that, on a weight-for-weight basis, it contains three times as much energy as petrol. It also has the advantage of providing up to 60% more efficient combustion than other fuels in internal-combustion engines. And, as a trump card, hydrogen combustion is virtually pollution-free — the principal combustion product being dihydrogen oxide, better known as water. The only objectionable products are oxides of nitrogen, a result of combustion in air.

At the moment, hydrogen usage is held back by its high cost and difficulty of storage, particularly in vehicles.

Storage as a liquid $(-253^{\circ}C)$, as a highpressure gas, or as a metal hydride presents problems of one kind or another, and the question of safety still needs resolving (remember the Hindenburg?).

Despite those problems, many scientists around the world see hydrogen as our future energy currency. Dr John Bockris, formerly of Flinders University in South Australia and now in America, has become well known for his books propounding the workings of a 'hydrogen economy'.

In Australia, Dr Wolf Sasse and his colleagues at the CSIRO Division of Applied Organic Chemistry are carrying out research on chemical reactions that produce hydrogen under the impetus of sunlight. Dr Doug Bradhurst of the new CSIRO Division of Energy Chemistry (formerly part of the Australian Atomic Energy Commission) is studying another class of reactions that do the same thing; he is also looking at the practicality of storing hydrogen in the pores of a spongelike alloy.

Apart from hydrogen, all feasible fuels release carbon dioxide into the air when burnt. By next century it is possible that concern about rising levels of carbon dioxide in the atmosphere will be another factor encouraging the large-scale adoption of hydrogen as a fuel. (See 'When the air's carbon dioxide doubles', *Ecos* 28.)

In our society we need electricity coursing through a grid to provide instantaneous power, and we need stored energy. This store provides fuel for transport and industry — and for electricity generation.

Proponents of the 'hydrogen economy' point to an advantage it would offer: ready conversion of electrical energy to stored energy and vice versa. When electricity is passed through water — electrolysis hydrogen is produced (and oxygen). When hydrogen is burnt in a power station or put into a fuel cell, electricity is generated.

Water-splitting

At present, the simplest way to produce large amounts of hydrogen is to electrolyse large quantities of water (it can also be made by reacting coal with steam and oxygen). Electrolyser plants operate at about 80% efficiency, and recent electrochemical research promises improvement of that figure. One of the avenues is to carry out the electrolysis at higher temperatures (1000°C or more) so that heat helps split the water.

However, huge amounts of electricity would be needed to produce the amounts of hydrogen required to replace today's petroleum usage. Australia's current electricity-generating capacity would have to be doubled to make enough extra electricity available to produce hydrogen equivalent to the petrol we now consume.

Because existing power plants have an efficiency of about 30% in converting heat from coal, oil, or nuclear fuel to electricity, the energy content of the hydrogen would be only about one-quarter of that of the fuel used to make the electricity. Hence, using solar energy, rather than electricity, to produce hydrogen has great attraction.

Indeed, Dr Sasse believes that the concept of the hydrogen economy only really makes sense when it is married to the use of a sustainable energy source — either solar energy or nuclear fusion.

In this way, our fossil fuels could be

The principal combustion product is dihydrogen oxide, better known as water.

preserved for applications where they cannot be replaced — for example, in the chemical industry. If solar energy is to win the day, what is wanted is a photochemical reaction that will efficiently break up water into its constituent elements and so allow the sun's energy to be stored in a convenient form.

Photosynthesis, which all green plants use to store sunlight in chemical form, is the prime example of a solar-powered photochemical reaction. With this living example before them, scientists have been challenged to see what they can come up with.

Dr Sasse and his CSIRO colleagues want, in fact, to create a test-tube analogue of a plant's photochemistry. Their aim is to develop a photochemical system that would produce a high-grade fuel (hydrogen) directly from solar energy. It would by-pass the need for cultivating, harvesting, and up-grading the primary product of photosynthesis.

When light impinges on the yellow solution, hydrogen bubbles forth into the collecting vessel. Dr Sasse and his colleagues are studying the performance of this ruthenium dye system with the aim of developing more effective and longer-lasting ones.



Thrusting spacewards — and hydrogenpowered.





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Already they have produced a hydrogen-oxygen mixture using light and an aggregation of complex chemicals, but the process still has a much lower efficiency than a plant's chloroplasts. And even that is rather modest; a typical forest converts stored energy to chemical energy with an efficiency of approximately 0.25%, and a field of sugar-cane does so at about 4%.

But, as plants show us, more important than efficiency is the stability of the system. Plants go on working year after year, but many of the man-made imitations work only for minutes. Dr Sasse's main concern is therefore to understand the factors that control the useful life of these systems.

The chemical systems are complex, with many types of reactants following particular chemical pathways. The problem is to prevent one chemical species disrupting the desired activity and pathways of the others.

The lifetime of species in Dr Sasse's apparatus is measured in 'turn-over numbers' — the average number of times a molecule carries out its wanted function (like absorbing a photon, or giving up a hydrogen molecule) before it is inactivated by some side reaction. Turn-over numbers therefore reflect both the life of a chemical and the yield of hydrogen.

Plants have a complex system of absorbers (or sensitizers), charge-separators, and energy transmitters and storages, and these provide the prototype for scientists such as Dr Sasse to mimic. Many chemical schemes have been described in the last few years. The most effective system produces a number of litres of hydrogen per day from each litre of solution, according to recent claims.

This is the one Dr Sasse is concentrating on, although he has studied a number of other systems. Basically, it involves a radiation-absorbing ruthenium complex (the sensitizer) reducing methyl viologen (paraquat), which in turn reduces water to hydrogen. To prevent the reaction from going backwards, ethylenediaminetetraacetic acid (EDTA) reduces the oxidized ruthenium complex, itself thereby changing irreversibly to an oxidized form. (EDTA is called a 'sacrificial' reagent, since it is constantly being used up. It is



A number of different chemical solutions can produce hydrogen under the action of sunlight. This is the one Dr Sasse and his colleagues are focusing on. The final result is the using up of EDTA and the production of hydrogen from water.

used to simplify the laboratory studies, and in a practical system would probably be replaced by a chemical that produced oxygen.)

How does your garden grow?

Plants use chlorophyll molecules and associated pigments to absorb quanta of radiation. These molecules act as 'antennae' for radiation of the appropriate wavelength — for most plants about 670 nanometres (a red colour), which corresponds to a photon energy of $1 \cdot 8$ electronvolts. In the ruthenium system, the ruthenium complex acts as light-absorber.

Photosynthesis, like all quantum-absorbing systems, exhibits a basic limitation in performance. All the photons with energy less than that needed for the required reaction are ineffective, while those with more than enough waste the excess. Nothing can be done to circumvent this limitation of quantum absorption, and solar cells and synthetic chloroplasts alike must necessarily live with it. So far, the best efficiency in capturing solar energy belongs to semiconductor materials (silicon cells win with 12–18% efficiency).

Once the sensitizer (chlorophyll or synthetic equivalent) has reached an excited state, a way must be found to store in a permanent form as much as possible of the energy it has absorbed. This is where the electron-transfer (or oxidation) reaction comes in. In the plant, the chloroplast transfers an electron across a water-oil boundary; in the case of the ruthenium system, methyl viologen and EDTA swap electrons.

The key is to prevent the reaction going backwards so that the excited state doesn't fall back without storing energy. As mentioned, the irreversible oxidation of EDTA prevents any backsliding in the chemical 'cocktail', and the long-lived excited state of the ruthenium bipyridyl complex also helps improve conversion efficiency. Intriguingly, the 'ratchet' in the plant cell is not conclusively known at present.

Dr Sasse and his team are continuing their investigations of the hydrogenproducing cocktail. They now know much more about the reaction pathways involved, and how to augment or block certain reactions. For example, they have found that adding small quantities of catalyst poisons (particular sulfur-containing compounds) to the system actually improves the yield and rate of hydrogen production. This seemingly paradoxical outcome occurs because the poison suppresses one of the major side reactions to a greater degree than it does the desired reaction.

The hydrogen-forming reaction is still a long way from being a practical proposition — in a small test tube only millilitres of hydrogen are produced — but the approach looks promising as the system's turn-over numbers are steadily improved. For example, suppression of side reactions has allowed the turn-over number of methyl viologen to be raised from about 100 to near 1000.

Comparing hydrogen with other fuels		
fuel	energy density	
	watt-hours per kilogram	watt-hours per litre
liquid hydrogen	33 000	2 300
petrol	12 880	9 0 00
metal hydride -FeTiH (2 · 5% hydrogen)	510	1 800
-MgNiH (4 · 5% hydrogen)	1110	1 500
lead-acid battery	30–50	

Liquid hydrogen is the most energydense liquid medium on a weight basis. On a volume basis, petrol is better. Further research is needed before we can say whether a stable system with a slow reaction rate is better than a relatively unstable system with a fast reaction rate. Cost, climatic conditions, and other related factors also enter the equation. Nevertheless, the prospect of hydrogen bubbling forth from a pond of chemicals exposed to the sun is certainly alluring.

Semiconducting electrodes

A similar sweet result is being sought by Dr Doug Bradhurst of the CSIRO Division of Energy Chemistry at Lucas Heights. Instead of organic materials, Dr Bradhurst uses semiconducting electrodes. Gaining his best result to date, he has constructed a titanium dioxide and platinum electrode system that, when immersed in water and illuminated with light, gives off oxygen and hydrogen at a rate that corresponds to 2% efficiency (a good figure considering the present state of the art).

The complete process looks just like electrolysis, except that the watersplitting energy comes from light instead of electricity (a similar series of electronexchanging reactions takes place). Actually, a bias voltage is necessary as well, to give the system that extra push needed to do the splitting, but electrical energy contributed from this source contributes only a little of the hydrogen energy generated.

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A small battery could do the job, but in the demonstration unit he has made Dr Bradhurst used silicon photocells to generate the needed voltage, so the unit is completely solar-powered.

Dr Bradhurst believes his scheme provides more hydrogen per dollar invested in plant than any other so far devised. Nevertheless, he is experimenting with other semiconductors to see whether he can improve the efficiency.

In principle, any semiconducting material can be used as an electrode, but in practice the range of materials with the right combination of physical and chemical properties is severely limited.

Ideally, the semiconducting layer should absorb light from the most energetically abundant part of the solar spectrum (photons with about 2eV of energy and above) so that most of the available radiation is absorbed. This energy level is sufficient to give rise to electrons at the



Dr Bradhurst and his solar-powered hydrogen-generator. It also produces oxygen.

illuminated electrode capable of splitting water.

Titanium dioxide is not an ideal material because it absorbs light only from the violet end of the solar spectrum, where photons have more than $3 \cdot 0 \text{ eV}$ of energy. Each of these absorbed photons can split water with energy to spare, but there are relatively few of them. This limits the maximum theoretical efficiency of sunlight-to-hydrogen conversion to about 3%.

Despite this disadvantage, titanium dioxide resists chemical attack much better than other semiconductors such as cadmium sulfide and silicon, which have better absorption figures. These latter materials are unsuitable for photo-splitting of water, as they themselves tend to break down.

Dr Bradhurst envisages that a titanium collector could form the basis of a combined solar hydrogen-generator and waterheater. The roof of an average house could accommodate a collector of 75 sq. metres, which at 2% efficiency collects a sizeable amount of energy. Six hours of sunlight could provide enough hydrogen to drive a small car 20 km. It would simultaneously also supply, through heat exchangers, sufficient heat to air-condition a house or to heat up a domestic swimming pool by several degrees.

Dr Bradhurst is pursuing lines of research that may uncover ways of improving the efficiency of the titanium electrodes. He is doping them with impurities of various other metals and trying altogether different materials for the electrodes. None so far has done as well as titanium.

Metal hydride sponges

No matter how cheaply we can manage to produce hydrogen, it's no good to us if we can't store the stuff. Storage in gasometers and in high-pressure pipelines is straightforward for industrial use, but how do we store hydrogen aboard cars and other vehicles?

Three storage possibilities are being entertained at the moment:

- ▶ as a liquid at $20K (-253^{\circ}C)$
- ► as a gas under high pressure at the temperature of the surroundings
- in gaps between metal atoms, a method being investigated by Dr Bradhurst (the National Energy Research Development and Demonstration Council (NERDDC) is supporting the work financially)

The first possibility, liquid hydrogen, requires very well-insulated cryogenic tanks, which for a car may cost about \$500. Even then, hydrogen will continue to boil off slowly, and the pressure of gas in the tank will steadily rise. If the car is not used daily, the gas must be vented off, creating both a waste of energy and, potentially, an explosion hazard.



When sun shines on the titanium dioxide electrode, hydrogen comes off the platinum electrode. A small auxiliary electrical force is required: a silicon solar cell does the job well.

A further drawback of liquid hydrogen is the quantity of energy needed to liquefy it. The magnitude of this energy penalty amounts to about 39% of the energy liberated by combustion of the hydrogen.

Compared with petrol, liquid hydrogen needs some 3 8 times more space for its containment; but then again, remember that on a weight basis hydrogen packs more energy, and it burns more efficiently.

Weight is, however, the main drawback with storing compressed hydrogen gas in cylinders. Because of the very high pressures involved, a steel cylinder of hydrogen containing as much energy as a tank of petrol would outweigh the tank by a factor of 30.



A hydrogen-powered engine under test at the University of Melbourne's Department of Mechanical Engineering.

Perhaps the foregoing explains why so much interest is being devoted to the storage of hydrogen in metal alloys in which a metal hydride forms. Some metals can store, at atmospheric pressure, 50% more hydrogen in their inter-atomic spaces than a container of equal volume filled with liquid hydrogen. However, the weight of the metal has to be reckoned with: in the most promising alloys it is 10–50 times the weight of the hydrogen.

This once more invites an odious comparison with petrol. Hydrogen stored as metal hydride is 10 to 20 times as heavy as a tank of petrol containing the same energy. Admittedly, in a comparison with the lead-acid batteries that may power an electric car, it fares much better. The hydride is 5 to 10 times better off on an energy-to-weight basis than the batteries.

The hydride forms when hydrogen under slight pressure contacts the powdered alloy. Heat is given out during this process. The reaction is reversed and hydrogen streams off when the pressure is released or heat is supplied to the system (or both). Some alloys need more encouragement — in the form of heat — to release hydrogen than others. However, nothing more than the heat contained in engine exhaust gases should ever be necessary.

For example, a hydride of iron-titanium alloy needs little more than a temperature of 60°C to exhaust it of hydrogen.

Dr Bradhurst has experimented with a magnesium-nickel alloy, which he found absorbed more than 4% hydrogen by weight; however, it needed temperatures of around 350°C to release the hydrogen. Such a temperature cannot easily be achieved from a motor vehicle's exhaust.

This is one reason he is devoting most time to researching the iron-titanium family of alloys, which sometimes contain small amounts of manganese. Although they absorb less than 2% hydrogen by weight, they have the advantage of needing little thermal stimulation to release the gas.

The alloy systems can be cycled repeatedly, although there is a risk of temporary loss of storage capacity if contamination with oxygen, nitrogen, water vapour, or carbon dioxide occurs. Dr Bradhurst found that even a brief (2-minute) exposure to hydrogen contaminated with 6% air caused an iron-titanium alloy to lose its absorption capacity rapidly and completely. Nevertheless, this situation can be remedied by exposing the poisoned alloy to pure hydrogen at high pressure (70 atmospheres) for an extended time.

Several iron-titanium alloys were prepared at Lucas Heights, and their properties were compared with those of commercial alloys. One such commercial sample came from the Daimler Benz Company in Stuttgart, West Germany, where the company is testing 28 vehicles that run on hydrogen or a combination of hydrogen and petrol.



The exhaust of a hydrogen-powered vehicle is largely water. It has been said that it's clean enough to drink.

The Division of Energy Chemistry plans to pursue investigations into metal hydrides further, with the long-term aim of developing superior alloys that could be manufactured on a commercial scale.

Practical test

Collaboration with the University of Melbourne on the development of a hydrogenpowered demonstration vehicle — a 4cylinder Cortina station wagon — is under way. The University's Departments of Chemical Engineering and Mechanical Engineering are building the vehicle with financial assistance from NERDDC.

The iron-titanium alloy from the Titanium Metals Corporation, U.S.A.,

that will be used in the van has been tested at the Division, and found to perform satisfactorily.

One of the big advantages motivating the vehicle's designers to specify metal hydride storage is the method's greater safety. After all, hydrogen is more dangerously explosive than petrol. In a televised experiment, incendiary bullets were fired into tanks of petrol, liquid hydrogen, and metal hydride. As you would expect, the tanks of petrol and liquid hydrogen both exploded spectacularly. However, the hydride burnt only along the path of the bullet.

Metal hydrides have one considerable disadvantage at the moment: their cost. The cost of the alloy needed for the Melbourne University station wagon exceeded \$2000, making a pretty pricey fuel tank. Dr Bradhurst is hopeful that continued research will find an alloy that is considerably cheaper.

And the cost of the hydrogen itself? Dr Bradhurst estimates that right now in Australia, electrolytic hydrogen produced with off-peak electricity would be cheaper than petrol. When petrol runs short and transport fuel is produced from coal, it will be cheaper to produce hydrogen from this source than liquid fuels.

Whether solar-produced hydrogen production will be technically feasible on a large scale, and economically attractive, remains to be seen.

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More about the topic

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