Q&A

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Hydrogen-fuelled buses already run in Berlin.

TECHNOLOGY

Hydrogen-fuelled vehicles

Louis Schlapbach

Hydrogen is hailed as a non-polluting synthetic fuel that could replace oil, especially for transport applications. The technology to make this a reality — particularly hydrogen-storage materials — has been a long time coming, but the first commercial vehicles might now be only a few years away.

Why would hydrogen be a good transport fuel?

Hydrogen is the lightest element in the periodic table, and so molecular hydrogen has the highest energy-to-mass ratio of any chemical. Indeed, that's why it is used to propel rockets, where it is essential to minimize the mass of fuel carried. Hydrogen is carbon-free, non-toxic, and its thermal or electrochemical combustion with oxygen yields nothing but energy and water — although its combustion in air might generate nitric oxide air pollutants in controllable amounts. Another advantage is that the main source of hydrogen is water, which is essentially an unlimited resource.

And what are the drawbacks?

The chief problem is that hydrogen is a gas at room temperature, so it takes up an impractically large amount of space. The gas must therefore be compressed in some way to make it compact enough for mobile applications. Another issue is less obvious: hydrogen is an energy carrier, not a source of energy. Unlike genuine sources of energy (such as solar radiation, fossil hydrocarbons, hydropower and nuclear power), hydrogen is not naturally available in sufficient quantities for widespread use, and must therefore be made by splitting water into hydrogen and oxygen. Splitting requires energy, whether in the form of electricity, light, heat or chemicals. But most of that energy is recovered when hydrogen is combusted.

Isn't hydrogen dangerously explosive?

In practice, no more so than petrol. People often think of the fire that destroyed the hydrogen-filled Zeppelin *Hindenburg* in 1937, and assume that the gas is dangerously combustible. In fact, the problem with the *Hindenburg* was its highly inflammable skin. It is true that mixtures of hydrogen and air burn over a rather broad composition range (mixtures in which 4–75% of the volume is hydrogen will burn; for comparison, mixtures of only 1–8% by volume of petrol in air will burn). Furthermore, hydrogen is more volatile than petrol, and diffuses faster through air. But comparative safety studies of fuel leaks from petrol- and hydrogen-fuelled cars, performed at the University of Miami, clearly demonstrate that hydrogen-fuelled cars pose less of a fire risk than petrol-fuelled vehicles.

What must be done for hydrogen to become a widely used fuel?

There are three crucial steps. First, economically viable methods must be developed to produce large quantities of hydrogen, ideally using renewable energy sources. Advanced water-splitting techniques that use electricity and some heat as energy sources are very energy-efficient, and might one day fit the bill. Second, hydrogen distribution and storage systems are required. Existing gas-distribution networks in cities and between industrial sites could be used to move large quantities of hydrogen around, but mobile hydrogen-storage vessels and filling stations are clearly necessary for transport applications. Several prototype hydrogen-filling stations already service fleets of hydrogen-fuelled buses, for example at Nagoya airport in Japan and in Berlin. But no countrywide hydrogen infrastructure has yet been set up — although Germany has developed a tool (called H2invest) for planning such an infrastructure. The third step is to develop technologies and devices for converting the chemical energy stored in hydrogen into more useful forms of energy. Currently, hydrogen can yield thermal energy in a combustion engine or electrical energy in a fuel cell (Fig. 1).

Could petrol-fuelled car engines be converted to use hydrogen?

Yes, by making minor modifications. But that's not a sustainable solution in the long term, as combustion engines convert chemical energy to mechanical energy (via thermal energy) with low efficiency. For example, the energy-conversion efficiency of a typical petrol-fuelled car in everyday traffic conditions is little more than 10%. Far more efficient would be a combined hydrogen-fuel-cell–electric-motor (Hy-FC-EM) system, known as a power train. But the development of an economically viable power train has proven far more difficult than was expected.

What are the problems in developing power trains?

There are three main issues. The first is cost — fuel cells generally require catalysts that contain rare and expensive elements. The second issue is that fuel cells have short lifetimes. Nevertheless, a few companies have successfully overcome these problems to develop potentially useful hydrogen fuel cells for transport applications. The remaining big hurdle is therefore to find compact, lightweight hydrogen-storage systems capable of delivering hydrogen gas to a fuel cell at approximately room temperature, and at pressures not much greater than atmospheric pressure. To stimulate research and development in this area, in 2002 the US Department of Energy set quantitative goals for the hydrogen content of storage devices (6% by mass by 2010, then 9% by 2015). So far, the targets haven't been met, and the new US government decided to cut its funding of hydrogen-storage research, opting instead to put more money into developing batteries for fully electric vehicles. However, the US House of Representatives has subsequently voted to restore most of this funding, and the energy department has revised the targets to 5.5% by mass for 2015.

Do the targets make sense?

No — the whole car needs to be optimized for mass, not just the fuel tank. In fact, many car manufacturers, owners and public agencies do not care if 1 tonne or more of mass is used inefficiently in heavy vehicles (which might weigh upwards of 2.5 tonnes). Concentrating efforts on the mass of the fuel tank alone is like asking an obese patient to lose weight from his left arm to control his total weight.

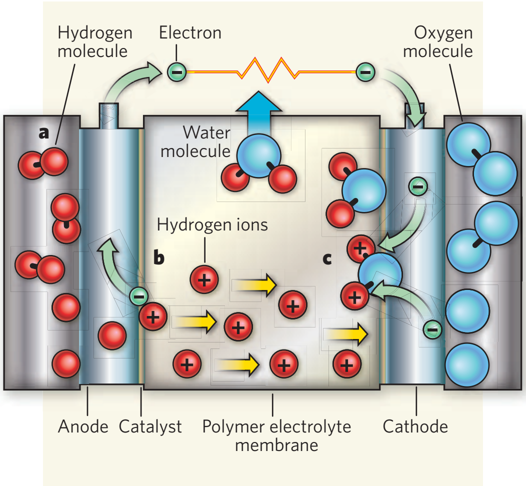

Figure 1 | A hydrogen fuel cell. Hydrogen is electrochemically combusted in fuel cells to produce energy. **a**, Hydrogen is channelled to the anode at one side of the cell, where the H_2 molecules split into hydrogen atoms. **b**, A catalyst lining the anode causes the hydrogen atoms to split into hydrogen ions (H^+) and electrons. A polymer electrolyte membrane allows the hydrogen ions to pass between the anode and the cathode, but the electrons must pass through an external circuit to reach the cathode, creating a current. **c**, Oxygen is channelled to the cathode, where it reacts with electrons and hydrogen ions to form water as the only side product. The water flows out of the cell.

How much hydrogen does a car need to store?

Using today's technologies, a safe, weight-efficient, five-seater car might weigh 1.2–1.5 tonnes. This would travel at least 500 kilometres on 30–35 litres of petrol or diesel, with the combined mass of the fuel and tank being 80 kilograms. To travel the same distance using a Hy-FC-EM power train, that car would need about 5 kilograms of hydrogen. The same car fitted with a hydrogen combustion engine would need 10 kilograms of hydrogen or more. The problem is that 5 kilograms of hydrogen at room temperature and pressure occupy about 56,000 litres — equivalent to a balloon 4.8 metres in diameter. Some method of squeezing this volume down by 1,000-fold is therefore essential.

Can't hydrogen be stored at high pressure, or liquefied, to reduce the volume?

Yes, but this isn't practical for hydrogen storage in cars. If hydrogen behaved like an 'ideal' gas, then a pressure of 100 megapascals (100 MPa, 1,000 times that of atmospheric pressure) would be needed to compress it to 1,000th of its volume at atmospheric pressure. But hydrogen exhibits ideal-gas behaviour only up to about 10 MPa; at pressures above 50 MPa, it deviates markedly from such behaviour, requiring even more pressure to compress it further. Also, the safety issues associated with storing the gas at those high pressures become a great concern. Compression of hydrogen above 100 MPa is therefore not a sensible option. Liquefaction certainly yields hydrogen in an extremely energy-dense form (as used for space technology), but the process requires temperatures below −250 °C. Such conditions, and the cryogenic techniques needed to obtain them, are demanding — but not infeasible — for ordinary petrol stations. The liquefaction process, however, also results in the loss of about 30% of the chemical energy of gaseous hydrogen.

So what else can be done?

Hydrogen can be reversibly absorbed or adsorbed (accumulated at the surface) by certain solid materials, greatly reducing its volume. The gas is then released on heating or on lowering the hydrogen-gas pressure. Two main classes of hydrogen-storage material exist, corresponding to two mechanisms of sorption: physisorption, in which H_2 molecules are weakly adsorbed by the material, but don't react chemically with it; and chemisorption, in which H_2 molecules react with the material's surface, dissociating into hydrogen atoms that are absorbed into the bulk, where they form metallic, covalent or ionic bonds with the material (Fig. 2).

What sorts of material adsorb hydrogen by physisorption?

Those that have high surface areas per unit of mass, such as some graphitic materials or high-porosity compounds. At full capacity, their hydrogen content can reach about 8% by mass. The problem is that, on planar surfaces (which occur in many materials) physisorption is weak. Temperatures below −200 °C (about the temperature of liquid nitrogen) are therefore generally needed to adsorb useful quantities of hydrogen. Physisorption is stronger in materials that have narrow, curved pores, and at surfaces decorated with hydrogen-attracting atoms. Zeolites (aluminosilicates) and metal–organic frameworks (complexes of metal ions and rigid organic molecules) might provide these features, raising the hope that hydrogen physisorption could one day be achieved at room temperature in such materials.

And which materials use chemisorption?

Hydrogen reacts with many materials — often metals or alloys, but also other compounds — to form hydrides that can be used as hydrogen-storage media. The reactions are often fast and reversible at practically accessible temperatures (20–100 °C), so that large amounts of hydrogen can be absorbed and then recovered. Materials that have been extensively studied for hydrogen storage include: hydrides of elemental metals (magnesium, palladium, thorium); hydrides of compounds that have the formula AB_5 (where A and B are usually metals), such as lanthanum–nickel hydride ($LaNi_5H_6$); and 'complex hydrides', such as magnesium–nickel hydride (Mg_2NiH_4) or barium–rhodium hydride ($BaRhH_9$).

How well do hydrides perform?

They easily reach hydrogen-volume densities far above that of liquid hydrogen, and can be recharged several tens of thousands of times. But because the host materials are not light, the quantity of hydrogen stored has not exceeded 4% by mass. To date, most of these compounds aren't practically useful for mobile hydrogen storage, as their hydrogen-storage capacities per unit mass are either too small or the temperatures required to release stored hydrogen are too high. But their volumetric hydrogen-storage capacity and their safety features are impressive.

Does that mean hydride research hasn't been fruitful?

On the contrary, there have been many useful discoveries from this field. Metal hydrides are now used as electrodes for batteries, such as those in commercially available hybrid cars. These batteries are safe, compact and quickly rechargeable. Metal hydrides also form the basis of certain temperature sensors in aircraft, and might one day be used in intelligent coatings that control the transparency of windows. Furthermore, hydrogen-induced pulverization techniques, discovered during the course of metal-hydride research, are now used to manufacture permanent magnets.

What's the latest thing in hydrogen-storage materials?

Current studies focus on solid-state storage using complex hydrides of light elements (those with low atomic masses), or high-pressure tanks (35 MPa) filled with such materials. These complex hydrides include alanates (which contain AlH_4^- anions, where Al is aluminium); borohydrides (which contain BH_4^- anions, where B is boron); amide hydrides (which contain lithium, nitrogen and hydrogen); and combinations thereof. They reach attractively high hydrogen contents of 8–20% by mass. For these materials, hydride formation and decomposition proceed over several steps through intermediate compounds. Experimental and modelling efforts are aimed at fine-tuning these reactions, and finding catalysts that speed up hydrogen release. Such efforts should yield materials that charge and discharge hydrogen in a temperature range of 20–100 °C; currently, temperatures of 300 °C or more are required. But practical applications of these materials are probably still a long way off. Another approach to hydrogen storage has also recently been resurrected, having previously fallen out of favour because of poor performance. In this approach, liquid hydrocarbons are used as a source of hydrogen gas. The process generates a dehydrogenated hydrocarbon side product, which could be re-hydrogenated at a recycling centre to generate more fuel.

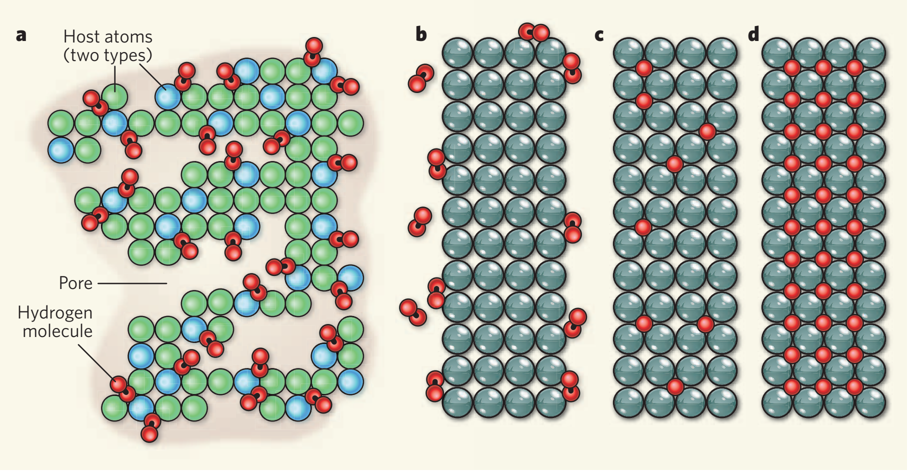

Figure 2 | Mechanisms of hydrogen storage. **a**, Materials that have high porosity store hydrogen using physisorption, in which the gas molecules accumulate at the surface of the material, but don't react chemically with it. **b–d**, Certain metals, alloys and other compounds store hydrogen using chemisorption. In this process, hydrogen molecules react with the surface of the material (**b**), where they split into separate atoms. Initially, the hydrogen atoms adopt random locations in the host material (**c**). They eventually form metallic, covalent or ionic bonds with the metal atoms to yield a hydride compound, in which the hydrogen atoms adopt a regular arrangement (**d**).

When will we see hydrogen-fuelled cars on the market?

Hydrogen-powered buses in Germany and Japan have already been successful, and about 50 prototype cars — both thermal-combustion and fuel-cell types — have so far been tested, with good results. I therefore wouldn't be surprised to see Hy-FC-EM cars for sale in about five years.

What are the other options for powering vehicles?

Given their current dominance, oil-based fuels will undoubtedly be used in vehicles for some time to come, although uncertainties about supply mean that their days are probably numbered. New types of rechargeable battery — safer lithium and lithium–air batteries, and higher-capacity metal-hydride batteries — will also raise the market potential of fully electric city vehicles and hybrid cars. It should be noted, however, that if most car owners switched to fully electric cars, many countries would need to double their electricity production. Similarly, hydrogen production also requires energy, such as electricity.

How will hydrogen compete with those other power sources?

This depends on trends in car design and the cost-effectiveness of hydrogen technology. Hydrogen-fuelled cars are already technically feasible, but if they are to be widely used, they must also be economically competitive with rival models that use other fuels. This will probably happen in a few years for smaller cars (those weighing about 1 tonne); a trend towards lightweight vehicles would therefore help to kick-start the market. But although car manufacturers increasingly use lightweight, high-strength materials, the average total mass of a car has continuously increased over the past decade, as vehicles grow in size, power, comfort and safety.

So what are the prospects for hydrogen as a fuel?

A weak trend towards customers preferring smaller vehicles does exist, and this will be strengthened as car price and fuel economy become more important to buyers. New safety devices that not only give drivers warnings, but also act directly on the car, should decrease the probability of accidents, reducing the need for heavy protection in vehicles. That would open the door to lightweight vehicles and so to hydrogen-fuelled mobility. Hydrogen therefore certainly has a place in long-term transport strategies. But to ensure success, the challenges ahead require smart goals and long-term support of the best scientists and engineers — not 'stop-and-go' politics from successive governments, as currently seems to be the case. ■

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