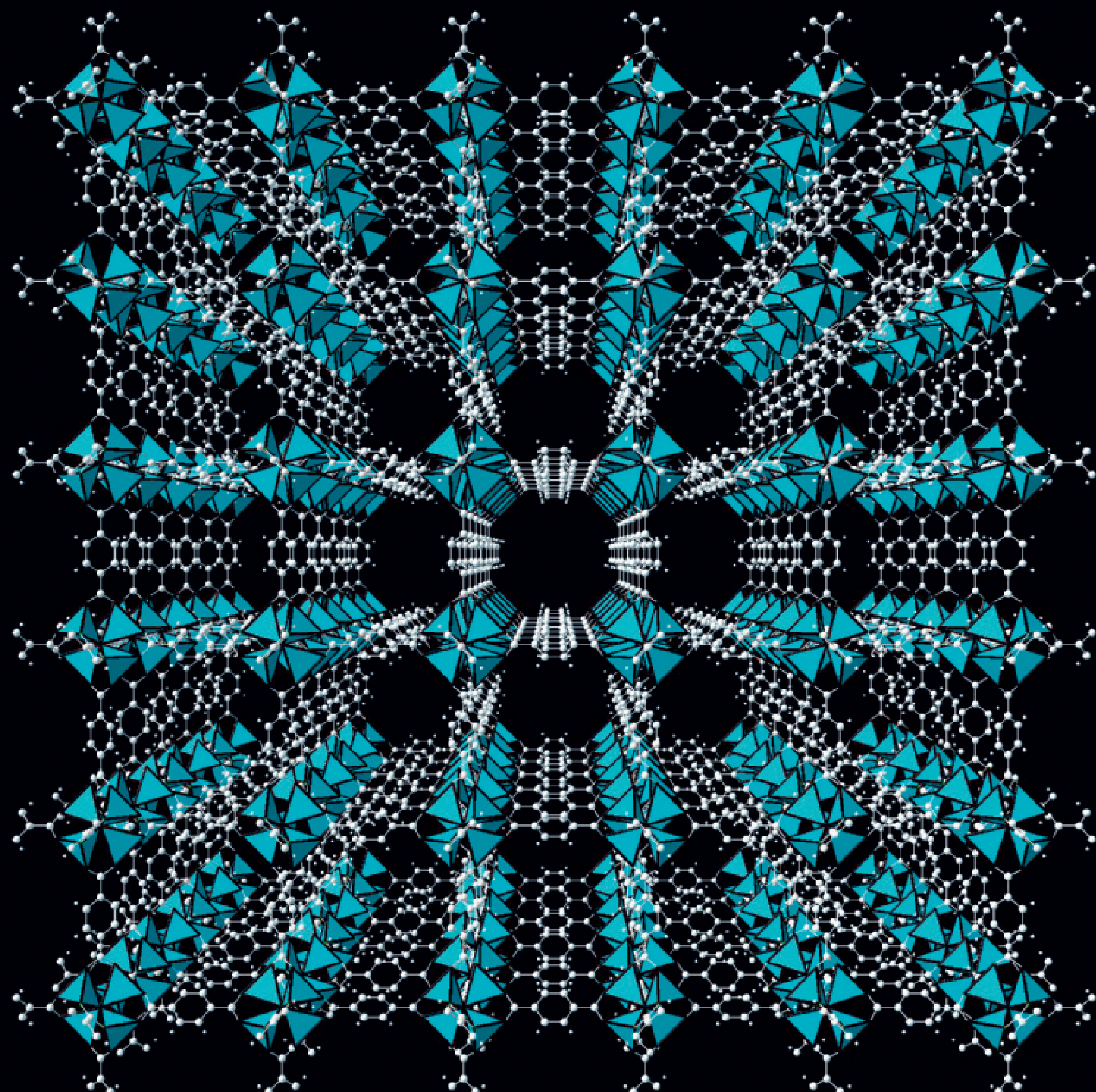


A lattice with lots of space for hydrogen: Metal-organic frameworks could store the fuel for fuel cell vehicles. They consist of metal compounds, shown as blue tetrahedrons, and bridges of organic molecules.

Photo: MPI of Metals Research – Michael Hirscher

The Miracle of Space in the Tank

Hydrogen could make driving a car cleaner – but there are currently no suitable storage materials for the gas. Researchers at the **Max Planck Institute of Metals Research**, the **Max-Planck-Institut für Kohlenforschung** (coal research) and the **Max Planck Institute of Colloids and Interfaces** are investigating the candidates for a hydrogen tank.

TEXT **TIM SCHRÖDER**

Sometimes there is a huge gap between desire and reality. The lecture theater was dead silent as Michael Hirscher presented the results of his laboratory experiments in November 2000. He had repeated these experiments for months, but the results remained the same: carbon nanotubes, until then much vaunted for hydrogen storage, were extremely reluctant to absorb hydrogen. Hirscher could only charge them with just under 2 percent by weight. More simply wasn't possible.

The publications by US researchers in respected journals had promised something completely different. They certified storage capacities of 10, sometimes even 67 percent by weight to the apparent miracle tubes – fascinating, hardly conceivable measurements. No question: the turn of the millennium was the era of the carbon nanotube. The carbon tubes were already enthusiastically feted as showing the way to the hydrogen future.

The downfall that followed was hard. And it began in November 2000 with a talk by Hirscher at a specialist meeting of the US Materials Research Society in Boston. Hirscher had gone through the experiment of his US colleagues in his own laboratory and established that the exorbitant hydrogen capacities were in no way due to the nanotubes, but were attributable in part to microscopically fine titanium fragments from an ultrasonic rod the US researchers used to prepare their tubes at the start of their experiments.

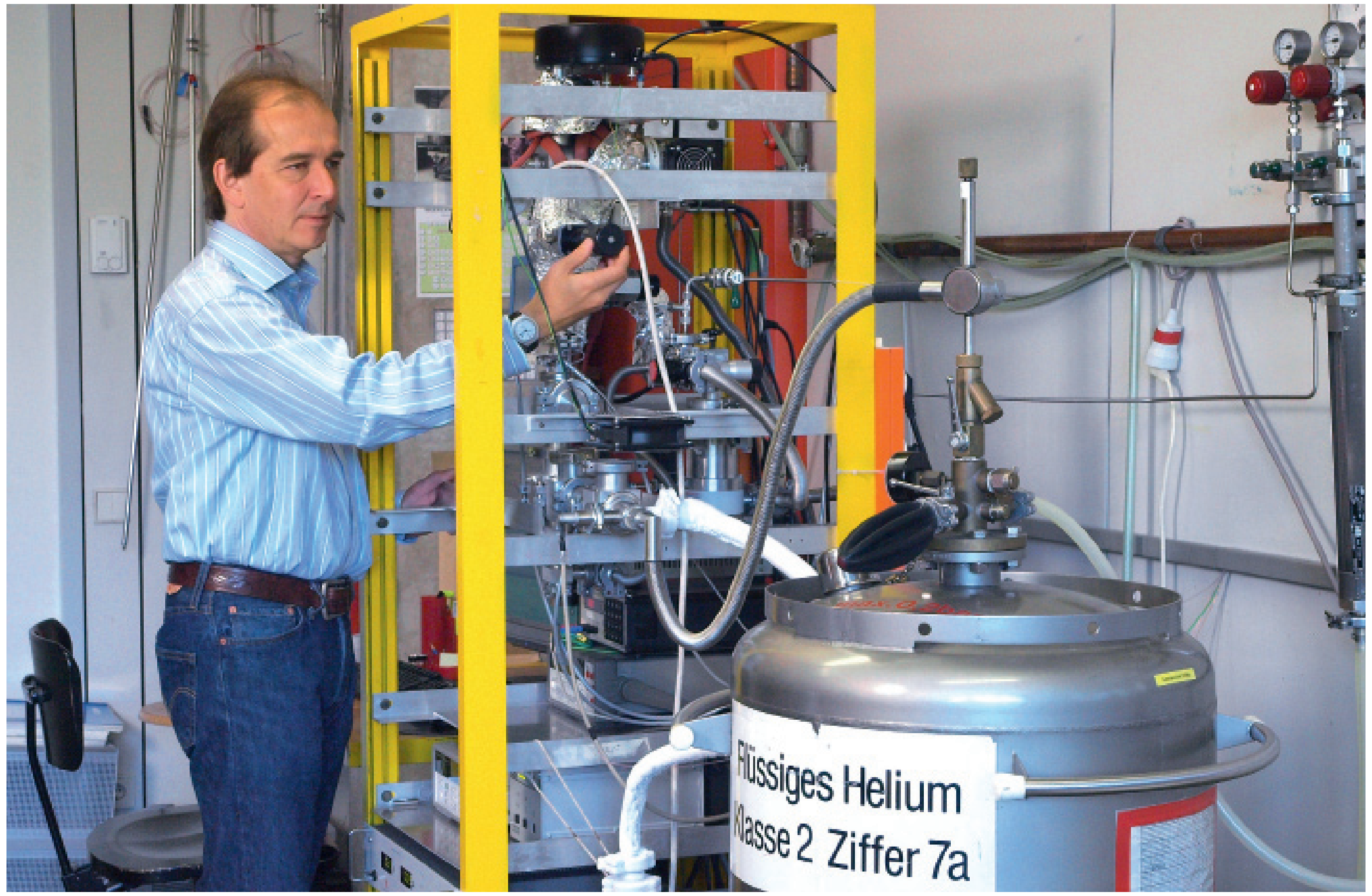
THE FUEL CELL VEHICLE IS THE YARDSTICK

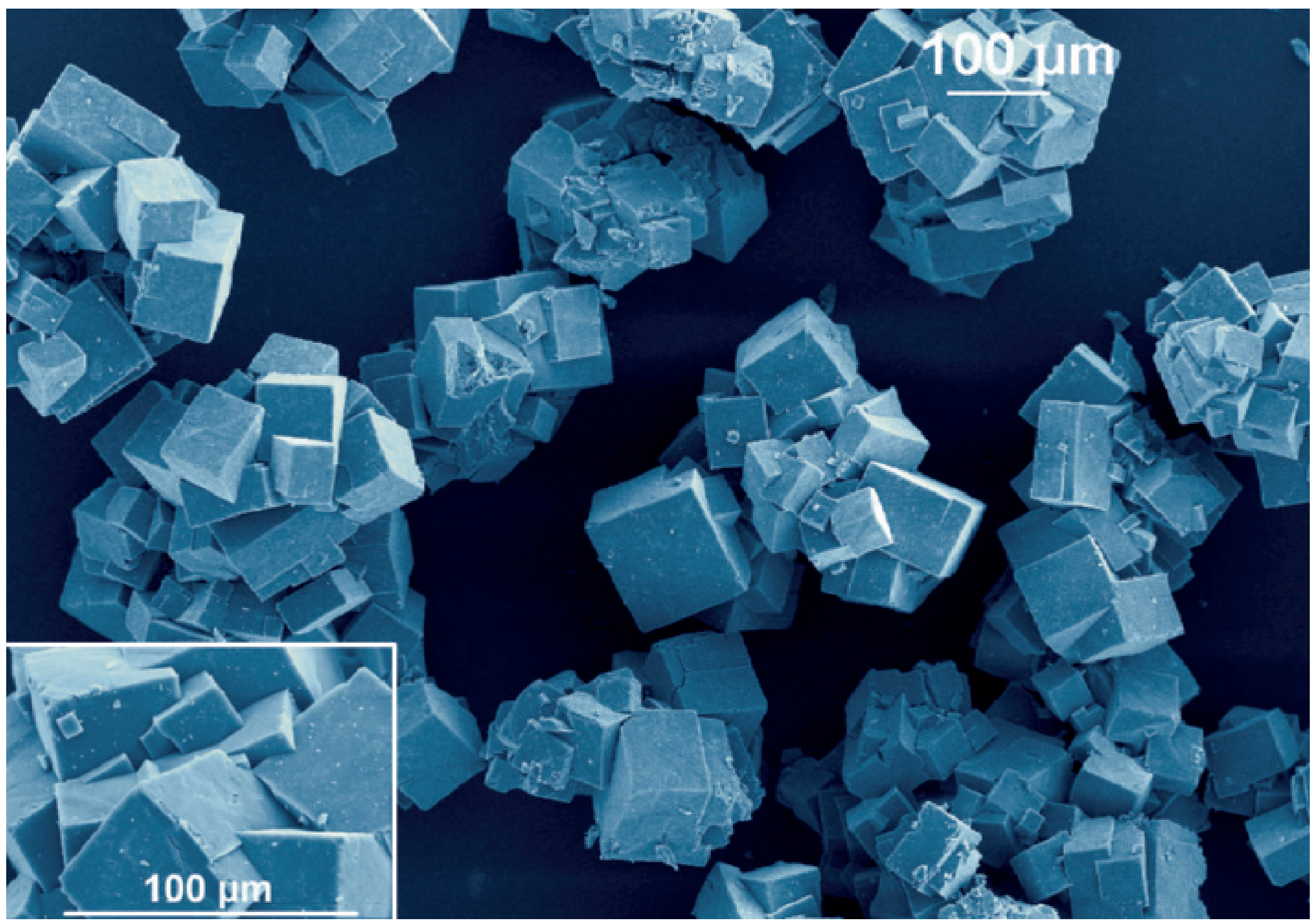
Hirscher's talk was a hammer blow as it explained that the unbelievable storage capacities resulted not from scientific brilliance but from incredible carelessness. The consequences were dire. The US Department of Energy cancelled the funding and took its leave from hydrogen storage in carbon nanotubes. Michael Hirscher's detective work, however, earned him the reputation of being the manager of one of the best analytical laboratories in the world.

Michael Hirscher is a physicist who researches the physics of metals at the Max Planck Institute of Metals Research in Stuttgart. Despite the sobering results, he continued with carbon for a long time. He meticulously checked what it could really do. "Today, we are convinced that carbon nanotubes really can't store much more than 2 percent by weight. And this is clearly not enough for the hydrogen future," says Hirscher.

The yardstick for hydrogen storage systems is the fuel cell vehicle, as this would open up the largest mass market to the energy-rich gas. The advantages are well known: in a fuel cell, hydrogen and oxygen molecules combine at a membrane to form water and thus generate electric power. The "smoke" from the exhaust is only hot steam. It doesn't get any cleaner than that.

Vehicle manufacturers have been testing hydrogen-powered vehicles for more than ten years. The vehicles have already traveled several million kilometers, but there is still a long way to go before mass production. And one of the largest obstacles is the hydrogen storage system. Although the energy density of hydrogen is around four times higher than that of gasoline or diesel fuel, hydrogen can, as yet, be stored in the vehicle only in heavy tank systems – so it's not really a compact solution. >





Photos: MPI of Metals Research – Bernhard Heinze (top)/MPI of Metals Research – Michael Hirscher (bottom)

top | The storage system that loves the cold: Michael Hirscher cools a material with liquid helium and charges it with hydrogen. He then uses a mass spectrometer to test how the storage material releases the gas when it is warmed up.

bottom | Cube with a lot of space for hydrogen – crystals of a metal-organic framework viewed with a scanning electron microscope.

High-pressure tanks that compress hydrogen to an impressive 700 bar, or 700 times atmospheric pressure, are the state of the art. Around five kilograms of hydrogen can be stored in this way. This allows a vehicle to actually achieve the operating range of 500 kilometers specified by car manufacturers. But these five kilograms require space: a high-pressure tank system like this one has a volume of roughly 260 liters, which corresponds to two voluminous suitcases that engineers must accommodate in the vehicle as inconspicuously as possible.

MIXTURE OF PET BOTTLE AND SUNTAN LOTION

Diesel vehicles need about 33 kilograms of fuel – around 37 liters – for the same distance. With all the necessary fittings and attachments, a suitable tank system for this has a volume of just 46 liters – as much as a small suitcase. To make matters worse, the 700-bar tanks are currently still very expensive. The requirements placed on the developers of hydrogen storage systems are thus: more compact, lighter and cheaper!

And it is exactly these requirements that Max Planck scientist Michael Hirscher wants to meet. For some years now, he has been putting his faith in MOFs: a strange, fascinating class of crystals. These metal-organic frameworks are undoubtedly different from other crystals. MOFs are a sort of hybrid creature between organic and inorganic chemistry, the world of plastics and the world of metals. Or, as some MOF researchers put it, “between PET bottle and suntan lotion.”

MOFs consist of a regular porous crystal lattice. Metal compounds, such as zinc oxide, which is added to suntan lotion as a protective pigment, are located at the corners of the lattice. The corners are connected via plastic-like molecular bridges, the linkers, which are familiar from PET beverage bottles. MOFs are very porous and surprisingly light. In the hand, they weigh as little as polystyrene granules – a 20-liter barrel can easily be lifted with one hand. Their porosity makes MOFs a promising alternative for storing hydrogen, since where there are many pores, there is also potentially a lot of space for hydrogen molecules.

The greater the number of pores or fracture edges running through a substance, the greater the surface area they offer in a minimum of space. And this is the issue for all modern storage materials, not only for MOFs: the larger the surface area, the more molecules can be adsorbed. MOFs achieve impressive values of up to 4,000 square meters per gram.

MEASUREMENTS AS GOOD AS AN OFFICIAL SEAL

In his laboratory in Stuttgart, Hirscher measures precisely how many molecules can be stored by an MOF. Gleaming barrels as big as wine casks filled with very low temperature liquid helium dominate the scene here. They cool the MOFs down to the operating temperature of minus 196 degrees Celsius because, as Hirscher and his colleagues discovered in a virtually endless series of measurements, hydrogen deposits in the MOFs primarily at very low temperatures.

Hirscher’s achievement is chiefly that he can measure minute amounts of MOFs that are sent to him by various research groups. A measurement in Stuttgart is tantamount to a seal of approval from a standards authority. MOFs are a relatively new class of substances that researchers became aware of only in the mid-1990s. When they discover new compounds, they can usually synthesize only a few milligrams. Hirscher often has to make do with less than a pinch of MOF for his measurements; generating reliable analytical results from this is an art. He has since worked out measurement procedures that very accurately register how many hydrogen molecules adsorb to the MOF surface at different temperatures.

The bond between the hydrogen and the MOFs is relatively weak. The molecules are not chemically bonded, but are held by physical forces, van der Waals forces, similar to blotting paper simply absorbing ink with its capillary force. This bonding to surfaces is called physisorption. Only at low temperatures and a pressure of about 20 bar is the kinetic energy of the hydrogen low enough to adsorb onto the MOF surfaces at all. MOF researchers all over the world are currently investigating what effect the pore size and different metals have on the bonding of hydrogen.

Hirscher collaborates with experts at BASF in Ludwigshafen, who can now produce kilograms of certain MOFs and who have been investigating MOFs since the mid-1990s. “MOFs have the advantage that one can create different molecules, and use a large number of metals to do this,” explains

> » The 700-bar tank is state of the art technology. The aim is to beat this.

Ulrich Müller, Research Director in Catalysis Research at BASF. "We can draw on a large pool of resources to design new, higher-performance MOFs." The best MOFs now store between 5 and 7 percent by weight of hydrogen. This is still not enough for a vehicle. At least 9 would be needed for them to be used in practice.

TANK WITH COMPLEX FITTINGS AND ATTACHMENTS

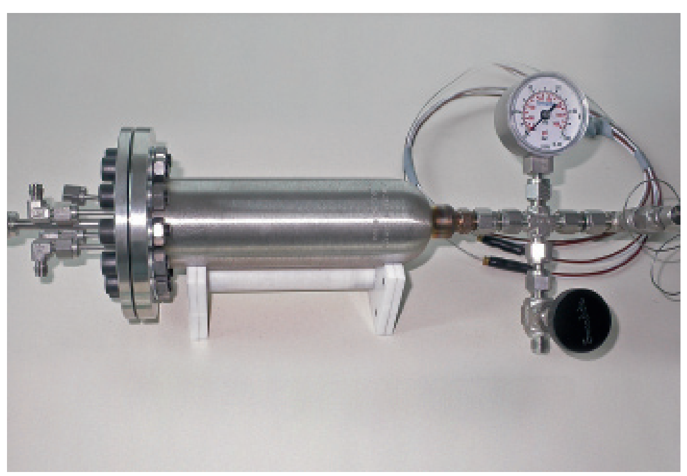
Nevertheless, Japan, in particular, is currently forging ahead with testing MOFs in prototypes – in its first tank systems, as the storage material is only one part of the whole story. If new types of hydrogen tanks are to be used in vehicles, the necessary fittings and attachments are also a must. And this is where all new storage concepts are still deficient. MOFs, for example, require their 196 degrees below zero. For the MOF car of the future, the hydrogen would thus first have to be cooled with liquid nitrogen when refueling. Moreover, the vehicle would require a hermetically sealed refrigeration tank, a cryotank. "The cooling consumes power and the cryotechnology would require additional space," says Hirscher. "If the system as a whole is considered, it becomes clear that today's MOFs do not yet perform sufficiently."

The 700-bar tank is state of the art technology. The aim is to beat this. This would indeed be possible, in principle, as hydrogen can be packed more densely into a solid-state reservoir, such as the MOFs, than in the gaseous state. The problem is that neither the MOFs found so far nor other compounds – the complex metal hydrides, for example – fulfill this goal. Michael Felderhoff and Ferdi Schüth at the Max-Planck-Institut für Kohlenforschung (coal research) in Mülheim an der Ruhr are working on these storage materials.

THE SEARCH FOR LIGHT METAL HYDRIDES

Metal hydrides consist of light metals and hydrogen that react together when a catalyst is added. Simple metal hydrides have been around for 30 years. And they are, in fact, already being used as storage materials – on modern submarines, for example, which switch to whisper-quiet fuel-cell operation when diving.

Storage material in the mill: Ferdi Schüth and Michael Felderhoff with a grinding jar in which they mill metal hydrides while at the same time testing their capacity to hold hydrogen.



The metal hydride tank, which was designed by the staff at the Institute of Energy and Environmental Technology using a sodium alanate from the researchers in Mülheim, is about 30 centimeters long and holds 2.6 grams of hydrogen.

Photos: MPI für Kohlenforschung (coal research)/Institute of Energy and Environmental Technology e.V.

A filling station for hydrogen is located in Hamburg-Hummelsbüttel. The municipal fuel cell buses also refuel here.

Photo: Vattenfall

At 2 percent by weight of hydrogen, the storage capacity of these compounds is severely limited. Around 250 kilograms of metal hydride are required to store 5 kilograms of hydrogen. In a submarine, which requires plenty of weight for the dive, the additional weight is very welcome. For vehicle manufacturers, however, which fight to save every gram of weight with aluminum bodies and magnesium sheets, the conventional metal hydrides are completely out of the question.

Felderhoff and Schüth are thus working on new complex metal hydrides in which they combine various metals. "We are trying to produce compounds of the light metals traditionally used, such as sodium and magnesium, with the so-called transition metals, such as titanium, which can bind more hydrogen," says Ferdi Schüth, Director of the Heterogenic Catalysis Department. In this case, the weight of the molecules hardly increases, while the storage capacity for hydrogen increases significantly.

STORAGE TEST IN THE BALL MILL

The manufacturing process seems strikingly simple: the researchers use ball mills in which balls hurling to and fro pulverize small pieces of light metal hydrides together with crumbs of transition metals. When the powder is fine enough, the transition metals slowly migrate into the light metal hydrides. Even while the milling is still in progress, the researchers can detect whether the newly obtained substance actually stores hydrogen reasonably well with the aid of small durable radio sensors in the mill. If an effective metal hydride is produced and hydrogen is bonded, the hydrogen pressure in the ball mill decreases.

Michael Felderhoff has already succeeded in producing complex metal hydrides of magnesium, calcium and aluminum, which store more than 9 percent by weight of hydrogen. The problem is that these compounds release hardly any of the firmly chemically bonded hydrogen again. In contrast to physisorption, the hydrogen molecule splits into two ions when it forms the chemical bond in the metal hydride, and these two ions are virtually incorporated into the hydride.

"Our aim is thus to create less stable hydrides that bind the hydrogen less firmly," says Felderhoff. But this is tricky, as some hydrides are then so unstable that they directly disintegrate again at room temperature and pres-

Markus Antonietti uses straw as the raw material to produce porous carbon storage material.

sure. So the Mülheim-based researchers work at higher pressures. “We hope to find complex hydrides that bind sufficient hydrogen at about 300 bar.” This is something of a magical limit, because vehicle tanks for 300 bar have been available for a long time. They are considerably cheaper than the newer 700 bar models and would therefore currently be more conceivable for serial use in cars.

And the metal hydride experts have to overcome a further hurdle: when metal hydrides absorb hydrogen, the chaotically moving hydrogen molecules undergo a transition into an orderly and thus low-energy state. This releases heat, which can increase the temperature of the metal hydride so that the reaction is reversed and the hydride decomposes into metal and hydrogen.

The heat released when refueling, however, would heat the material to several hundred degrees. A vehicle fuel tank would require huge heat exchangers to dissipate the heat. Much too heavy. But Felderhoff even hopes to get a grip on the heat problem using new unstable metal hydrides – because if hydrogen atoms are more loosely bonded, less binding energy is released.

The Institute of Energy and Environmental Technology in Duisburg has designed prototypes of hydrogen storage systems with metal hydrides. In their search for the optimum hydrogen catcher, Felderhoff and Schüth also work closely with the research center for alternative propulsion at General Motors in Mainz-Kastel. “We are pleased about this collaboration – after all, the Mülheim-based working group is the most outstanding group in the world for complex metal hydrides,” says GM Project Manager Ulrich Eberle. Eberle and his colleagues are currently pushing ahead with all three storage technologies at the same time – the 700 bar tank, the MOFs and the complex metal hydrides. The car maker is also developing its own storage materials.

USING THE LUNGS AS A MODEL FOR REFUELING A CAR

“With a 700 bar tank, a hydrogen-powered car already has a range of 500 kilometers – about two to three times as far as with battery operation,” says Eberle. “Our aim, however, is to further increase the energy density of the tank with new technologies, but we can’t say with certainty right now which technology is the best.” GM has already built its first test tanks, demonstrators, with which the new materials are tested. “We want to know how well and, above all, how fast the different materials absorb hydrogen and release it again – and how often they survive such refueling cycles,” says Eberle.

For vehicle use, it is crucial that the storage system absorb and release hydrogen quickly. No one would enjoy waiting 15 minutes until the MOF or metal hydride has finally been filled. Markus Antonietti, Director at the Max Planck Institute of Colloids and Interfaces in Potsdam-Golm, believes that storage in metal hydrides and MOFs could be thwarted at this hurdle. Metal hydrides must first chemically bond the hydrogen, which takes some time. And as for the MOFs: “If you want to charge a crystal with a gas, all molecules must migrate from the outside through the pores to deep inside,” says Antonietti. This limits the speed of the gas exchange.

The chemist is thus working on porous materials that have a hierarchical construction, similar to the human lung. The gas initially permeates through large openings deep into the material, where it penetrates into increasingly finer branches, like in the bronchial tubes.

Photos: Norbert Michalke/iStockphoto

According to the researcher, this type of biomimetic, or nature-inspired, system can be charged with gas within seconds. Of course, which storage technology will finally win the race is an open question, even for Antonietti.

CARBON FRAMEWORK FROM THE SAUCEPAN

In any case, his porous carbon storage materials have the advantage of being very inexpensive and can easily be produced in large quantities. Antonietti’s raw material is straw, 20 million tons of which pile up in Germany every year. For the complex metal hydrides, on the other hand, an inexpensive metal compound must yet be found. What Antonietti does with the straw is “gourmet cooking.” For several hours, the straw must lie in water simmering at 200 degrees. Additives, such as foaming agents, ensure that the bubbles remain stable and don’t collapse again. The result is a solid, porous carbon framework. Antonietti calculated that around one hundred kilograms of porous carbon should be sufficient for one vehicle tank. And the local straw would easily be sufficient to equip the annual fleet of three million new cars in Germany.

None of the technologies is fully developed yet – neither the biomimetic carbon nor the MOFs nor the metal hydrides. But the achievements are remarkable – and the gap between desire and reality with regard to hydrogen storage is thus gradually closing. ◂

GLOSSARY

MOF – Metal-Organic Framework
Metal compounds are linked via organic molecules to produce a very light material with large pores.

Van der Waals forces
Interactions between atoms and molecules that are not based on a chemical bond. In a narrower sense, the forces created when molecules such as hydrogen molecules are distorted by the random movement of the electrons to form dipoles.

Binding energy
The energy released when a chemical bond is formed. In order to break a bond, the energy must be expended again. The stronger the bond between two atoms, the higher the binding energy.

Complex metal hydrides
Compounds of light metals, such as sodium and magnesium, and transition metals, such as titanium and hydrogen.