

SPACE INVADERS

Space exploration usually means leaving Earth's orbit. But chemists are now burrowing inside solids to open new vistas. **Katharine Sanderson** reports from the internal frontier.

Solids have a reputation for permanence and reliability. Astronauts and sailors rejoice in returning to solid ground. And few things are more durable than solid gold. Unlike their flightier cousins, the gases and liquids, solids have regular structures that generally resist deformation. But there are materials that challenge our notions of a solid. They are rigid and strong, yet flexible, incredibly light yet so porous that the surface area of one gram could cover an entire football pitch.

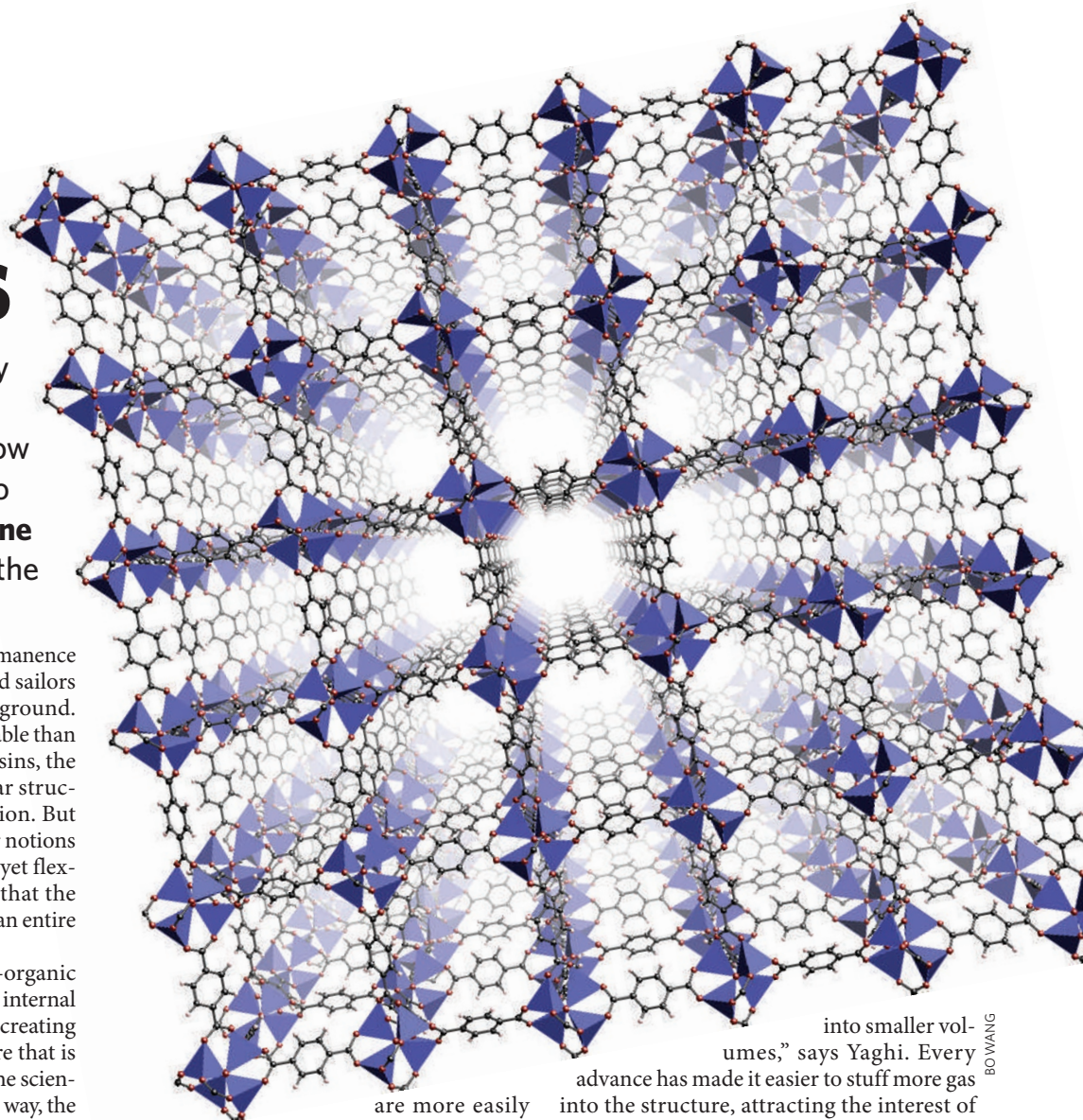
These solids are known as metal-organic frameworks, or MOFs. They have no internal walls, just a bare molecular scaffold, creating a regular, sturdy, crystalline structure that is packed full with empty space. But if the scientists building these structures get their way, the materials will soon be packed full of useful gases, such as compressed hydrogen or methane, making it easier to store and transport these alternative fuels.

Chemists expected that the vast, open structures of MOFs — more air than solid — would collapse readily. Yet the structures can be designed such that they are held together entirely by strong chemical bonds — carbon-carbon, carbon-oxygen or metal-oxygen. They are composed entirely of joints, made from metal oxide units, and struts, which are organic groups. As long as those metal oxide joints don't shear or buckle under pressure, the structure stands firm, like builders' scaffolding.

Structural gymnastics

The resulting wall-less structures produce solids that are incredibly light with very low densities — sometimes as low as 0.2 gram per cubic centimetre — allowing a chunk of the material to float on water. Some cleverly engineered MOFs can even flex and bend slightly without collapsing.

With all that space to play with, these solids



are more easily penetrated than most. Chemists have used porous materials, including clays and zeolites, to trap and store gases for decades. But the pores and channels in naturally occurring porous materials are of varying sizes, so researchers have sought to make porous structures with uniform openings. In trying to construct such materials in the 1990s, Omar Yaghi at the University of California, Los Angeles, hit on a recipe for making frameworks with precisely controlled pore sizes. In 1998, Yaghi engineered the first MOF structure by mixing together two molecular building blocks — namely metal oxide and organic groups¹.

Since then, researchers have created materials with larger and larger pores. In doing so, they have repeatedly broken records for internal surface area in solids, and for low density, making zeolites look stodgy by comparison. But record-busting is not the only motivation to get bigger surface areas. "It's not just an obsession of mine to get higher numbers, it's the way to compact more and more gases

into smaller volumes," says Yaghi. Every advance has made it easier to stuff more gas into the structure, attracting the interest of German chemicals giant BASF, which is about to move its MOF research into small-scale production.

Yaghi is thrilled by BASF's investment in his work. In Yaghi's lab, MOFs can now be constructed to order. He has compiled a list of metal fragments to act as the scaffold joints, and a compatible range of organic links. If these linking groups are linear — that is with connecting points on both ends — they can be used to make chains or cube-like structures. More exotic networks can be made from triangular or square groups with connectors sticking out from each corner.

BASF supports another MOF chemist, Gérard Férey at the Lavoisier Institute in Versailles, France. Férey claims to hold the world record for the internal surface area of a MOF², published in 2005, at 5,900 square metres — or, the same area as an average-sized football field — for every gram of material. His material was built from triangular groups of chromium atoms linked together by terephthalic acid molecules.

"The limits are in our imagination."
— Gérard Férey

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Yaghi could soon beat Férey's record. His latest MOF — MOF-200 — looks likely to have a whopping surface area of 8,000 square metres per gram, once the synthesis is complete. But Mark Thomas, an expert in porous solids at the Newcastle University, UK, cautions against reading too much into these claims, which are based on calculations developed for materials with much smaller pores, and with internal walls. "It's a pore volume converted into a surface area," he explains, "it is an apparent surface area." Férey agrees. "The numbers don't represent anything physically," he says. "We have to find a new definition for the surface of very large pores."

Still, Yaghi says that the numbers do have meaning, and they can be used to compare MOFs with each other and with other porous materials. The surface area of a single layer of porous carbon, when calculated in a similar way, comes out at a relatively tiny 2,600 square metres per gram.

Storage space

Yaghi's hopes for trapping and storing gases within the cavernous space provided by MOFs are focused on hydrogen storage. Hydrogen offers a low-polluting alternative to petrol as a fuel for road vehicles, but it faces many technical and infrastructure barriers. Not least of these is storing enough hydrogen on a vehicle in a safe and affordable way.

The US Department of Energy says the ultimate hydrogen car will need enough fuel for a 480-kilometre trip, and yet the fuel tank must not be too heavy or too bulky. It has set a target of 2010 for a viable storage system in which hydrogen makes up 6% of the system's total weight. In addition, the system has to operate over a range of "expected ambient conditions" — storing and releasing hydrogen at temperatures between -30°C and 50°C and at a maximum onboard operating pressure of 100 bar.

None of the existing options achieve this. Conventionally, hydrogen has been stored as a gas by keeping it in a high-pressure canister, or stored as a liquid at a chilly 20 kelvin (-253°C). But high-pressure tanks are bulky, and liquid hydrogen is expensive to keep cool. In principle, porous materials can increase the amount of hydrogen stored in a given volume, without relying on extremely high pressures or low temperatures.

In the late 1990s, carbon nanotubes generated much excitement as a way to store hydrogen. Researchers in industry and academia claimed storage levels ranging from 3% to 10% by weight at ambient temperatures and pressures. But most of these results — including one claim that graphite fibres can adsorb their own weight in hydrogen — have not been repro-



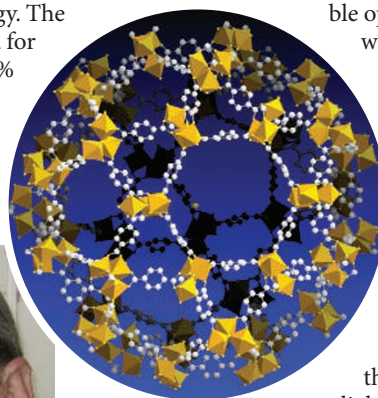
Chemical creations: Omar Yaghi was the first to design a metal-organic framework.

duced. Researchers are now more cautious of spectacular claims about hydrogen storage.

Today's front-runners for hydrogen storage in materials are metal hydride systems. These operate on the principle of chemisorption — whereby hydrogen is trapped by forming a chemical bond with the material, so forming a metal hydride. They operate at moderate pressures, but the material needs to be heated to release the hydrogen, thereby consuming more energy. The current storage record for metal hydrides is 9% by the weight of the material alone, but the Department of Energy's target includes the fuel tank



Inside story: Gérard Férey's metal-organic framework (right) is credited as having the largest internal surface area.



and accessory parts in the calculations, so that value translates into just 4% by weight for the overall storage system.

A different process, known as physisorption, is responsible for the weak electrostatic attractions that hold gases inside MOF pores. Weak interactions mean that releasing the gas from the material requires less energy — nothing like that needed to break chemical bonds. "The good thing about physisorption is that it's easily reversible," explains chemist Matthew Rosseinsky from the University of Liverpool, UK. And the great thing about MOFs that enhances that easy reversibility is their openness. "Things move in and out with great facility," says Yaghi.

For now, though, trapping hydrogen in MOFs still requires low temperatures. Although MOFs need pressures of only 70 bar to get hydrogen into the materials, they typically need temperatures around that of liquid nitrogen, at 77 kelvin — to keep them there. This is because of the weak interaction between hydrogen and the scaffold. As it starts to warm up, the energy in the system breaks the interactions, leaving the hydrogen free to exit the framework.

Out cold

Yaghi claims the record for hydrogen storage in MOFs. He says that at 77 kelvin, and at a pressure of 70 bar, his MOF-177 material can store 7.5% hydrogen by weight³. Although that sounds promising, carrying tanks of liquid nitrogen as well as hydrogen is not a viable option. "That's not very practical when you want to run an automobile," Yaghi admits. And even at these temperatures, MOF-177 still misses the 2010 target — which sets a goal for the material alone of 9% by weight.

Yaghi is optimistic about achieving the 2010 target with a MOF that can operate at room temperature. Férey is more sceptical. He thinks that the first step should be to move to slightly warmer temperatures: "If we reached 150 kelvin instead of 77 kelvin it would be a great improvement."

And recent work has challenged the idea that bigger pores are always better. Martin Schröder at the University of Nottingham, UK, has calculated the optimum pore size for stuffing hydrogen into a MOF — with the surprising result that medium-sized, rather than giant, pores were the winners⁴. With smaller pores, the thinking goes, the scaffold is more curved, improving its chances of interacting with gas molecules.

N. K. YAGHI

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It is the lure of engineering MOF structures to enhance these interactions that attracts Yaghi. If MOF structures could be tweaked to strengthen physisorption, they might be able to operate at higher temperatures. But this is a delicate art: if physisorption is too weak, the hydrogen won't stick, yet as it increases more energy is needed to release the gas. What's needed is something in between a physical electrostatic interaction and a chemical bond.

Weighty advantage

Yaghi proposes modifying the organic groups in his MOFs by adding a light metal such as lithium. The extra electrons provided by lithium would strengthen the interactions between the gas and the MOF. Yaghi predicts that by simply adding some lithium into his system he could improve the current room-temperature record of 1% hydrogen by material weight to 4%.

Others are exploiting MOF's ability to flex and bend to create clever hydrogen-trapping devices. Thomas and Rosseinsky and their colleagues constructed a cylindrical MOF from a network of large cavities separated by small windows⁵. The windows are too small to let hydrogen through. But when the structure is completely dried out under vacuum, it can flex and the windows open slightly so that hydrogen can enter. As the pressure is raised to 1 bar, roughly atmospheric pressure, more hydrogen stuffs into the cavities, attaching itself to the scaffold and making it more rigid. This forces the windows to close, trapping the hydrogen inside. At this point, the pressure can be reduced to as low as 0.01 bar and the inherited rigidity keeps the hydrogen trapped.

This all takes place at the temperature of liquid nitrogen, but it means that when the temperature is raised, the windows can open again and set the hydrogen free. The system is not perfect by any means, admits project scientist Darren Bradshaw, at the University of Liverpool, noting the low storage level achieved so far: just 1% by weight. But, he says, "it's a proof of principle that small windows that dynamically open are a good way to store hydrogen".

If MOF technology is going to be a serious contender for hydrogen storage, industry needs to get involved, not least for scaling-up produc-



Cheaper, cleaner: compressed natural gas is becoming an increasingly popular fuel source worldwide.

tion. MOFs are not yet cheap, easy things to make. They also contain metals, which can be expensive. This is where BASF comes in.

BASF has been involved in MOF research for eight years and has switched its activities from the research division into BASF's daughter company, BASF Future Business in Ludwigshafen, Germany. "The transfer from academia to industry is really a tough job," says

BASF project manager Thomas Danner. Researchers need only small amounts of product, so the solvents and starting materials can be more expensive than those used in industry.

In the short term BASF is not looking at MOFs for storage of hydrogen, but rather for natural gas or methane. "So many questions remain to be answered for the hydrogen economy," says Danner. Natural gas, however, is an existing market, with millions of vehi-

cles running on compressed natural gas (CNG) already on the roads. Today, most CNG vehicles are used for public transport, and buses can tolerate the bulky storage tanks and shorter driving distances. But as the number of CNG vehicles grows, BASF predicts that longer driving distances and lighter storage will become key demands.

More importantly, MOFs can trap complex gases, such as methane, more easily than they can hydrogen. These gases have more electrons available to interact with both the organic and

metal groups. Existing MOFs can store methane and carbon dioxide at room temperature, circumventing one of the biggest challenges of hydrogen storage.

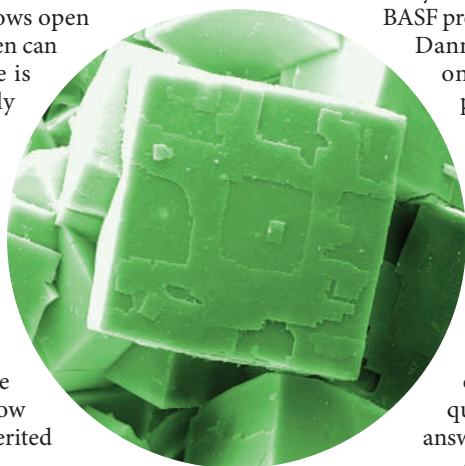
Scaling up

BASF can now make kilograms at a time of MOFs. Danner says that the development stage will last until at least 2009, at which point he expects to see a MOF product on the market. The challenge is not necessarily the technology, but finding the right market for the right product. According to Danner, adding MOFs to a standard CNG fuel tank operating at 200 bar pressure can already increase the distance travelled with a single tank by 25%, but he sees no reason why this cannot be increased to 45% in future.

For now, the practical potential of these super-sponges seems as vast as the space they contain. And whether MOFs ultimately deliver on their gas-storage promise, or disappoint, as carbon nanotubes did, researchers will find other uses for them. For example, their ability to absorb large amounts of guest molecules makes them ideal for catalyst applications. Férey remains amazed that almost no research has been done on MOF catalysis. He is also developing a biomedical MOF for delivering vast quantities of drugs to the bloodstream, while Yaghi is pursuing carbon dioxide storage in MOFs. "It's the very beginning, the limits are in our imagination," says Férey. ■

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How solid is this? The cavities inside metal-organic frameworks can easily adsorb gases.

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