Molecular Sponges for Hydrogen Storage

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November 2023

1. Introduction

Metal-organic frameworks are fairly recent inventions, but I have written about them before, just not in this context. These materials are composites of molecules that are very good at absorbing gases, and my previous post involved carbon dioxide. The earlier post is described and linked below.

A Curious Journey to an Old Friend: *I normally don't cross over the border to cover Canadian Startups, but this company (Svante) is heavily invested in U.S technology and personnel as well as venture capital. They also appear to have a well-developed process similar to one developed by UC Berkeley working with ExxonMobil on an eight year project. I reported on the UCB-EM project in 2020, and that is the old friend.*

Svante's technology: Solid sorbents, particularly metal-organic frameworks (MOFs), are a step change for the carbon capture industry. Their energy efficiency, resistance to degradation in the face of post-combustion flue gas impurities, and low cost of ownership make them ideal for carbon capture. That's why Svante's team of scientists and engineers elected to use them in the first place.

https://energycentral.com/c/ec/curious-journey-old-friend

As you can tell from the title, this paper is about hydrogen storage. My primary source is an article in a recent Science issue referenced below.

2. The Challenge with Hydrogen

Hydrogen seems like the perfect fuel. By weight it packs more punch than any other fuel. It can be made from water, meaning supply is almost limitless in principle. And when burned or run through a fuel cell, it generates energy without any carbon pollution. But hydrogen takes up enormous volume, making it impractical to store. Compressing it helps, but is expensive and essentially turns hydrogen storage tanks into high-pressure explosives.[1]

Now, a molecular sponge made of organic compounds and cheap aluminum promises a practical solution, holding significant amounts of hydrogen at low pressures. Described in a paper accepted last week at the Journal of the American Chemical Society (JACS), it is the latest in a series of promising metal-organic frameworks (MOFs), and it suggests that the materials could be close to a mass market application, serving as fuel depots for backup power sources at industrial operation.

"For the first time ever, we have sorbents that are potentially cheaper than compressed gas in a realistic application," says Hanna Breunig, a chemical engineer at Lawrence Berkeley National Laboratory who helped analyze the economics of using the aluminum MOF. To Omar Farha, a chemist at Northwestern University who wasn't involved in the new work, it shows that "this field is progressing at a really incredible speed.

[1] Robert F. Service, Science, Volume 381, Issue 6665, "Molecular 'sponges' could be hydrogen fuel tanks," Sep 28, 2023, https://www.science.org/doi/epdf/10.1126/science.adl0643

Hydrogen is already in wide use as an industrial chemical, and storage has been a long-standing problem. The primary solution to date has been to compress hydrogen at up to 700 bar, some 50 times the pressure of an outdoor grill's propane tank. But the high-pressure tanks are costly, and energy-guzzling compressors are needed to fill them. And even then, a liter of hydrogen compressed to 700 bar stores less than one-fifth of the energy of a liter of gasoline.

Some researchers are exploring storing hydrogen in underground caverns carved out of salt formations—but that geology is rare, and subterranean microbes might eat up the hydrogen. Compounds such as metal hydrides or ammonia can store hydrogen chemically. But these compounds must undergo reactions to unshackle the hydrogen, and recharging the material can be difficult.

MOFs are now emerging as an alternative. These porous solids look like molecular Tinker-toys. Metal atoms serve as hubs that are tied together with organic linkers—carbon-bearing molecular chains. The result is a chemical cage with passageways and voids that trap gases injected under mild pressures. When the pressure is lifted, the hydrogen flows back out.

In 2014, Jeffrey Long, a chemist at the University of California (UC), Berkeley, and his colleagues reported a nickel-based MOF that could store a record amount of hydrogen: 23 kilograms per cubic meter, about half as much as a high-pressure tank, but without the danger and expense of added pressure. An MOF not only needs to soak up lots of hydrogen; it must also release it easily. The ideal binding strength—measured as the heat of absorption—is be-tween 15 and 25 kilojoules per mole of hydrogen (kJ/mol). Below that range the grip is too loose, and the natural energy of hydrogen is enough for it to wriggle free of the cage. Above that range, the grip is too tight, and the system must be heated to push hydrogen out. "It's like a Goldilocks zone," says Hayden Evans, a chemist at the National Institute of Standards and Technology.

The nickel-based MOF has a near ideal binding energy of 14 kJ/mol, because the nickel atoms attract the slightly polar hydrogen molecule through weak electrostatic forces...

Competition is now rising from aluminum, which costs just over 1/10 as much as nickel. In 2022, Anthony Cheetham, a UC Santa Barbara chemist, and his colleagues laid the groundwork when they reported an aluminum-based MOF that looked promising for capturing carbon dioxide. The aluminum MOF requires less energy to release the captured carbon than more conventional liquid carbon-capture compounds…

Now, in the JACS paper, Cheetham, Evans, and colleagues have tested the aluminum MOF for hydrogen storage. It stores just two-thirds as much gas as the nickel MOF. And with a binding energy of just 8.6 kJ/mol, it must be chilled to about –100°C to store its maximum amount of hydrogen. Nevertheless, Cheetham says the raw materials are so cheap that he expects the MOF to cost just $2 per kilogram. That would easily beat a $10 per kilogram community goal for the production cost of MOFs made from nickel and other more expensive metals. "It's hard to imagine any MOF being as cheap as this one," says Zeric Hulvey, who heads hydrogen storage at the U.S. Energy Department's Office of Energy Efficiency and Renewable Energy.

The modest storage capacity means the new MOF isn't likely to work for storing hydrogen in fuel cell vehicles, where volume and weight are critical constraints. However, the combination of low cost, mild operating pressures, and a manageable cooling requirement already points to a practical use, Hulvey says: storing hydrogen for backup power sources that could replace diesel generators at industrial operations, such as data centers…

Author's comment: The above described MOF might also be able to store hydrogen at electric vehicle refueling stations. See the post below for some more information on these, and their big brothers (same name as the referenced post).

Hydrogen Hubs: For roughly the last month or so, I've danced all around the subject / title of this brief paper with the posts referenced below. However, I've seemed to do this without bringing these together, as this post will do.

So what is a hydrogen hub? It is a major user of green hydrogen that will use renewable electricity from the grid to produce adequate supplies of green hydrogen via an electrolyzer and store this hydrogen in high pressure tanks. The storage might have several functions:

- The electrolyzer can be sized based on average demand rather than peak demand.
- Storage potentially disassociates times of production and use to allow the electrolyzer to use the least-cost renewable electricity for the former when it's available.
- Stored hydrogen can be used for backup when there is an electric outage.

https://energycentral.com/c/ec/hydrogen-hubs

Note that the above referenced paper has many other references to other related papers.

3. Hydrogen Storage & Delivery

Storage and delivery are tightly related for incumbent technologies. Both require compressing hydrogen as much as possible. For storage this is a no brainer, but for delivery this is not quite as obvious. Pipeline-delivery requires moving as much hydrogen as possible through a pipeline, which can usually done by compressing the hydrogen at the sending end, expanding it during transit, and perhaps, compressing it again upon receipt for higher-pressure storage, or use lower-pressure MOF-storage

There is a hybrid hydrogen transit method – by tube-trailers. Tubes are long, high-pressure (180 bar or ~2,600 psig) storage or transit tanks (see below). An evolution of this method might involve lower-weight "tubes" based on Aluminum MOF Technology.

Gaseous hydrogen can be transported through pipelines much the way natural gas is today. Approximately 1,600 miles of hydrogen pipelines are currently operating in the United States. Owned by merchant hydrogen producers, these pipelines are located where large hydrogen users, such as petroleum refineries and chemical plants, are concentrated such as the Gulf Coast region.[2]

Transporting gaseous hydrogen via existing pipelines is a low-cost option for delivering large volumes of hydrogen. The high initial capital costs of new pipeline construction constitute a major barrier to expanding hydrogen pipeline delivery infrastructure. Research today therefore focuses on overcoming technical concerns related to pipeline transmission, including:

- *The potential for hydrogen to embrittle the steel and welds used to fabricate the pipelines*
- *The need to control hydrogen permeation and leaks*
- *The need for lower cost, more reliable, and more durable hydrogen compression technology.*

Potential solutions include using fiber reinforced polymer (FRP) pipelines for hydrogen distribution. The installation costs for FRP pipelines are about 20% less than that of steel pipelines because the FRP can be obtained in sections that are much longer than steel, minimizing welding requirements.

[2] Energy.gov, Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen Pipelines, https://www.energy.gov/eere/fuelcells/hydrogen-pipelines