



## Energy Focus

New simulations suggest cost-effective materials design for H<sub>2</sub> storage

Before hydrogen can be fully exploited in alternative and “clean” fuel systems, such as fuel-cell vehicles, these systems need a cost-effective, energy-efficient way to store and deliver the hydrogen at desirable temperature and pressure conditions. Now, researchers have proposed an inexpensive material design that appears able to store and deliver bulk hydrogen (H<sub>2</sub>) at an unprecedented rate. They report their findings in a recent issue of the *Journal of the American Chemical Society* (doi:10.1021/jacs.6b08803).

When sufficiently cooled or pressurized, hydrogen can exist as a liquid. But compressing it into a fuel tank at room temperature (25°C) poses an expensive challenge. Binding H<sub>2</sub> to specially designed host materials offers an option for storing more gas at lower pressures and higher temperatures. Still, current candidate materials bind H<sub>2</sub> through weak van der Waals forces and can only take up 10 g/L, a mere 25% of the US Department of Energy’s uptake target for hydrogen storage, as discussed in the Office of Energy Efficiency & Renewable Energy fuel-cell technologies multi-year research and demonstration plan.

Now, Jose Mendoza-Cortes, assistant professor of chemical and biomedical engineering at Florida State University, has proposed several materials that may solve this problem. He systematically explored how different candidates might bind H<sub>2</sub> efficiently and effectively—at pressures ranging from a vacuum to 700 atm—based on simple models and adsorption theory.

“Our initial hypothesis for a good H<sub>2</sub> storage material was that we need an interaction energy of 15–20 kJ/mol for the H<sub>2</sub> interacting with the material,” Mendoza-Cortes says.

A porous, crystalline framework made from lightweight organic elements that form strong covalent bonds comprises the basic structure. Mendoza-Cortes proposed that by bonding transition-metal elements inside these covalent organic frameworks, or COFs, their affinity for

H<sub>2</sub> would increase. Previous work had used precious metals in a similar way to increase adsorption capacity; in contrast, this study uses abundant metals.

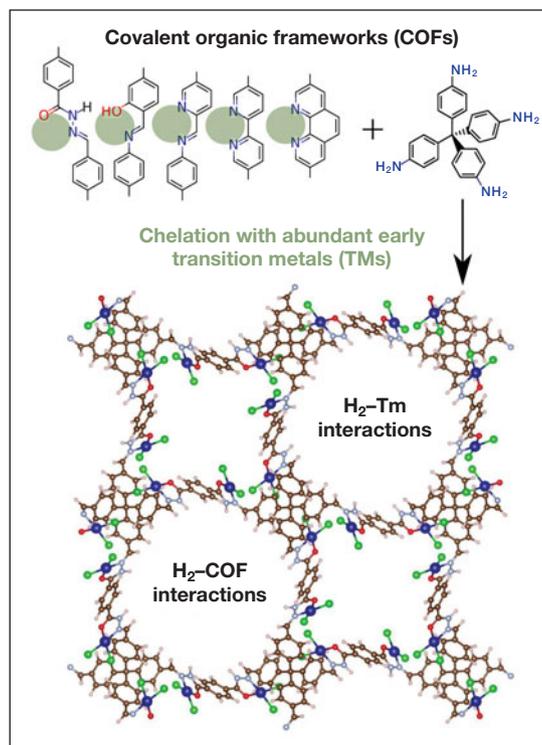
“The COFs themselves are not good for H<sub>2</sub> storage; their available interactions with H<sub>2</sub> are weak,” Mendoza-Cortes says. “Stronger interactions are obtained from transition metals interacting with H<sub>2</sub>.” These interactions arise from quantum mechanical forces between the molecules.

He simulated several hundred combinations of transition-metal-doped COFs to determine their H<sub>2</sub> uptake capacity. The complex model of “thousands of atoms and millions of configurations” revealed optimal configurations for binding transition metals to COFs. The pore size and small distance between metal sites allow H<sub>2</sub> to interact with all the transition metals in adjacent layers, resulting in a cooperative effect.

“The results were surprising ... because we have tested this hypothesis with precious transition metals before, but we did not expect to have superior results by using cheaper and more abundant early transition [metals],” Mendoza-Cortes says. He suggested that cobalt-, nickel-, and iron-based COFs would take up the most H<sub>2</sub>; up to 40 g/L at 700 bar and 25°C.

Importantly, Mendoza-Cortes found that there is a preferred binding site for each material where the storage is most effective. For example, one configuration of a cobalt-based framework (COF-301-CoCl<sub>2</sub>, see figure) reached a total of 30.5 g/L of H<sub>2</sub> at 120 bar. While 8.3 g/L of the stored bulk H<sub>2</sub> could be attributed to pressure alone, the extra 22.2 g/L comes from the material structure itself. This optimal or “sweet spot” region had not been fully explored before.

“Showing the great promise of utilizing COF materials doped with abundant, first-row transition metals for H<sub>2</sub> storage opens many new possibilities for



Covalent organic frameworks (COFs) doped with transition metals take up extra H<sub>2</sub> over a range of pressures. Credit: *Journal of the American Chemical Society*.

people to design and synthesize novel porous materials,” says Wei Zhang, an associate professor in the Department of Chemistry and Biochemistry at the University of Colorado Boulder, who was not involved in this study.

Fixing the transition metal inside the framework poses the main barrier to actually synthesizing the materials. Economically viable mass production presents another obstacle. Still, given the predicted performance enhancement, the transition-metal frameworks have the potential to be economically and practically viable.

“The low price of early transition metals and more practically useful temperature ... would greatly facilitate further development of organic-based porous materials for efficient H<sub>2</sub> storage,” Zhang says.

Mendoza-Cortes plans to explore whether he can apply this systematic, theoretical design approach to other problems in energy storage or chemical separation. The fundamental understanding provided by this study offers a promising application for computational materials design.

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