U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

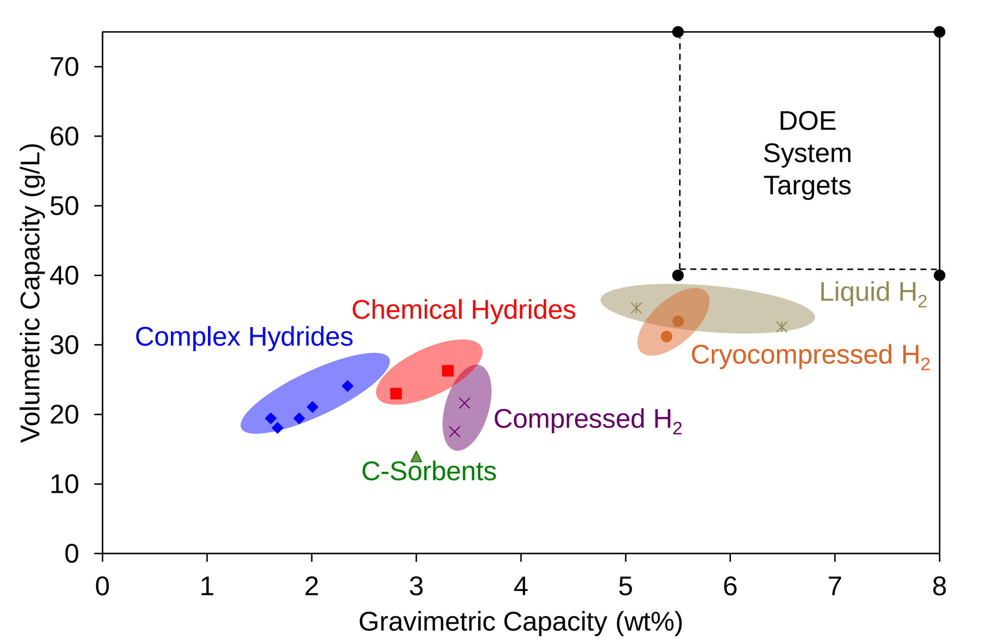
Metal- and Cluster-Modified Ultrahigh-Area Diamond Network Materials for the Ambient Temperature Storage of Molecular H_2

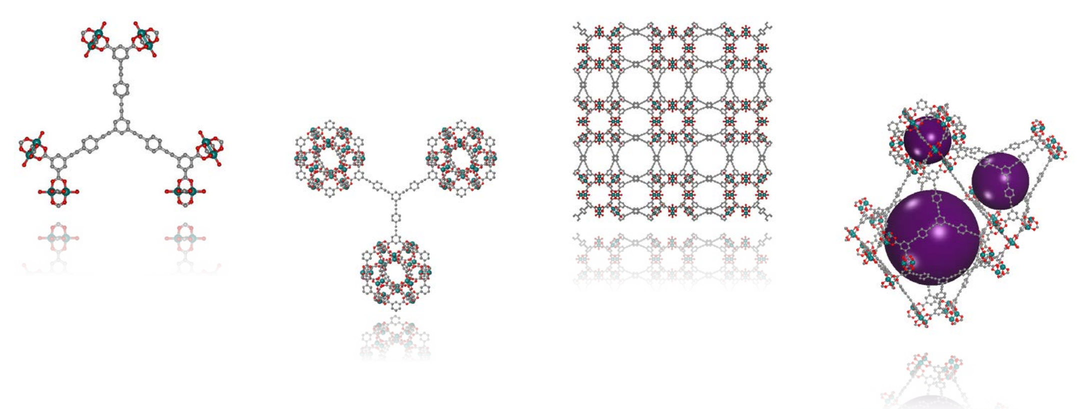
Joseph E. Mondloch, Omar K. Farha and Joseph T. Hupp

Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208

Background and Introduction

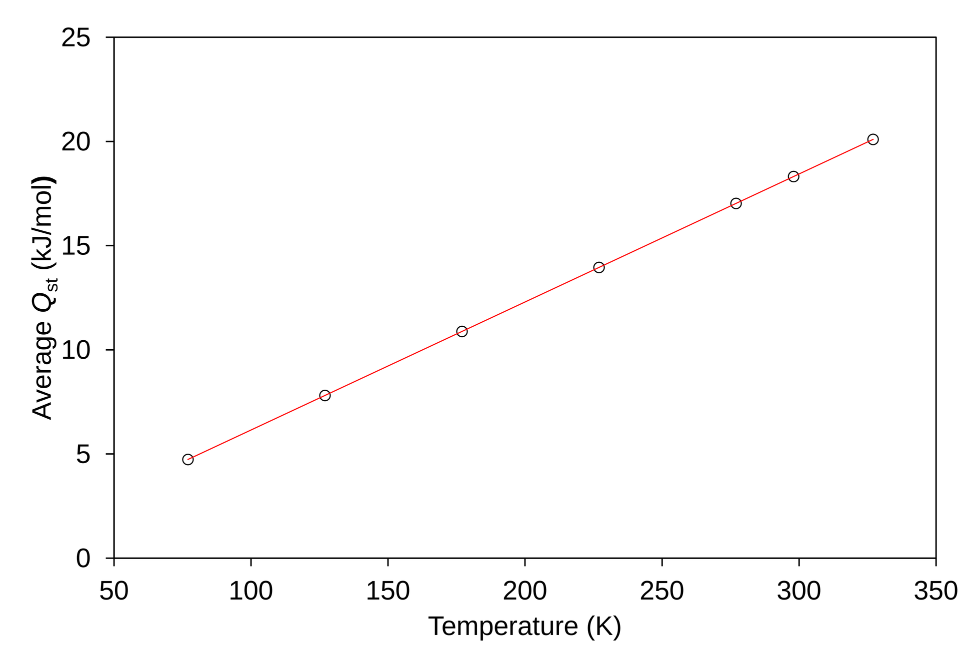
- Molecular hydrogen (H_2) is an attractive alternative energy source that can potentially replace hydrocarbon technology.[1]
- A crucial challenge to enable H_2 as an energy carrier is the development of suitable storage materials.
- Both chemical (typically dissociative) and physical (non-dissociative physisorption) sorption-based strategies are being actively pursued to overcome this challenge.[2]





- However, their typically low isosteric heats of adsorption (Q_{st}) require that H_2 be stored at cryogenic temperatures (e.g., 77 K).[4]
- A key experimental challenge to implement ambient temperature H_2 storage (in physisorption-based sorbents) is to increase their Q_{st}.[5]
- *One very promising strategy to achieve the desired Q_{st} is to incorporate stable, but coordinately unsaturated, divalent metal cations into ultrahigh-area sorbents!*

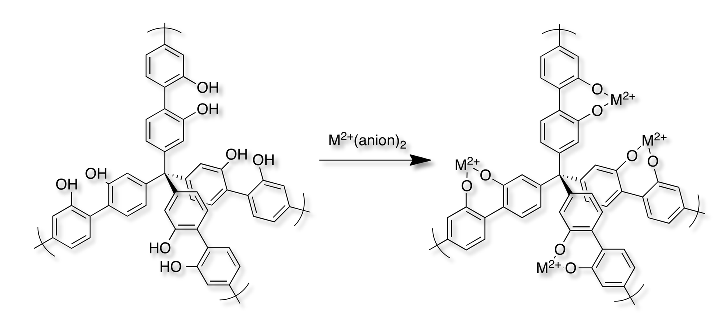
- Ultrahigh-area (> 3,000 m^2 g^{-1}) physisorption-based sorbents approaching the DOE's gravimetric and volumetric system targets have been developed (e.g., NU-100).[3]



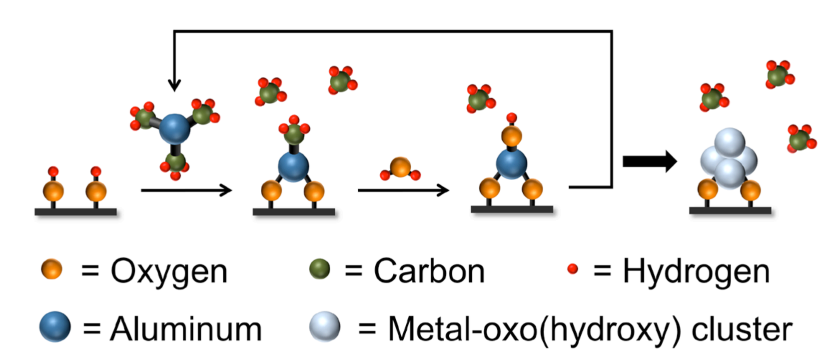
[1] Schlapbach, L.; Zuttel, A. *Nature* **2001,** *414,* 353. [2] Reproduced from: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/tech_status.html. [3] Farha, O.K.; Yazaydin, A.Ö.; Eryazici, I.; Malliakas, C.D.; Hauser, B.G.; Kanatzidis,M.G.; Nguyen, S.T.; Snurr, R.Q.; Hupp, J.T. *Nature Chem.* **2010,** *2,* 944.

Approach

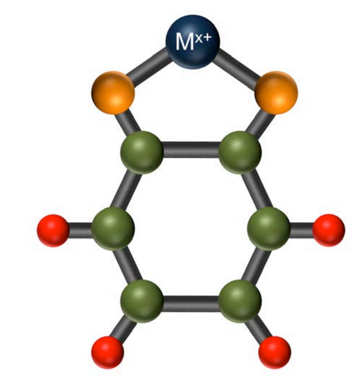
- An ultrahigh-area diamond network material (PAF-1 @ 5,600 m^2 g^{-1}) was recently reported by Ben et al..[6]
- PAF-1 will be functionalized with a varying number of –OH or –NH_2 groups per cavity and subsequently divalent metal cations.



- Small metal-oxo(hydroxy) clusters will be deposited onto functionalized PAF-1 derivatives via atomic layer deposition.

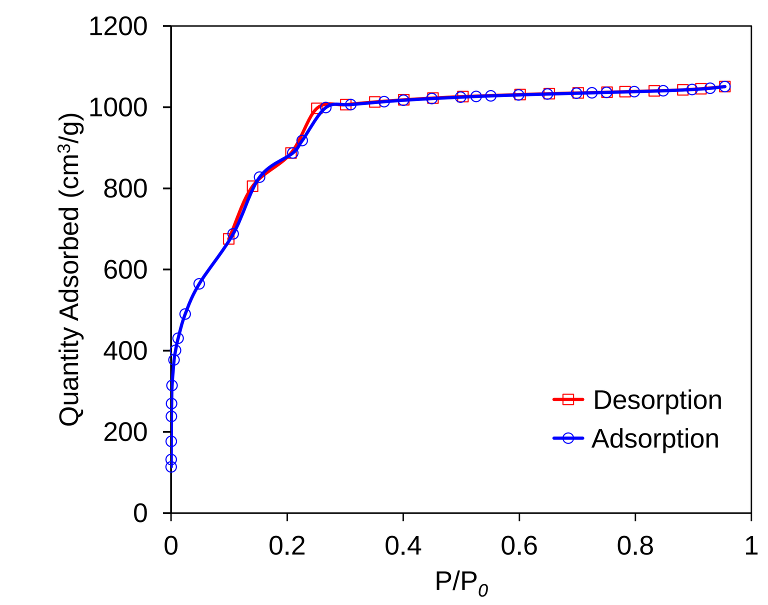


- Given the large number of potential materials, we will utilize computational guidance from Prof. Randall Q. Snurr to target the most promising Q_{st}.[7]

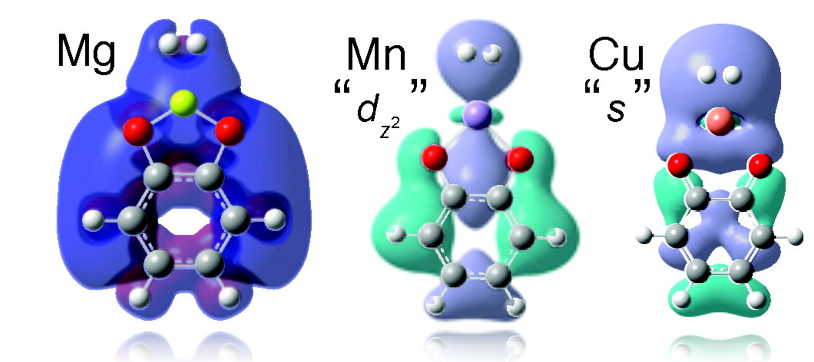


Metal	Q_{st} (kJ/mol)
Li^+	-10
Mn^{2+}	-20
Mg^{2+}	-22
Ni^{2+}	-78
Cu^{2+}	-84

- Metalated PAF-1 derivatives will be characterized by ICP-OES, gas sorption measurements and XAFS (among others).



- Despite ambitious computational efforts,[7] little experimental data exists regarding the detailed mechanism(s) of enhanced H_2 sorption.



- In collaboration with Dr. Jeff Miller at the DOE's ANL and APS, we will utilize XAFS to probe the local atomic structure of the metal- and cluster-modified PAF-1 derivatives under dynamic conditions.

[4] Bhatia, S.K.; Myers, A.L. Langmuir, 2006, 22, 1688. [5] Simpson, L. "U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Program Hydrogen Sorption Center of Excellence: Materials Go/No-Go Recommendation Document" **2009,** 1-41. [6] Ben, T.; Ren, H.; Ma, S.; Cao, D.; Lan, J.; Jing, X.; Wang, W.; Xu, J.; Deng, F.; Simmons, J.M.; Qiu, S.; Zhu, G. *Angew, Chem. Int. Ed.* **2009,** *48*, 9457. [7] Getman, R.B.; Miller, J.H; Wang, K.; Snurr, R.Q. *J. Phys. Chem. C* **2011,** *115,* 2066.

Impact

This project aims to synthesize, characterize and evaluate a new class of materials, namely metal- and cluster-modified ultra-high area diamond network materials. If fully successful, these materials are potentially capable of satisfying, and even exceeding, the U.S. DOE's 2015 excess gravimetric and volumetric H_2 storage requirements at ambient temperature (to start, on a "materials only" basis). In addition, by utilizing *in operando* XAFS measurements, we aim to obtain a predictive understanding of the mechanism(s) by which enhanced H_2 sorption is realized. Such insights promise to help guide the next generation syntheses of improved sorbent materials.

Acknowledgments

This research was supported in part by the Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Awards under the EERE Fuel Cell Technologies Program administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by the Oak Ridge Associated Universities (ORAU) under DOE contract number DE-AC05-06OR23100.

Modified Physisorption-Based Materials for the Ambient Temperature Storage of Molecular H_2