

IV.H.1 From Fundamental Understanding to Predicting New Nanomaterials for High-Capacity Hydrogen/Methane Storage and Carbon Capture

Taner Yildirim^{1,2}

¹Department of Materials Science and Eng.
University of Pennsylvania
Philadelphia, PA 19104

²National Institute of Standards and Technology, NCNR
Gaithersburg, MD 20899
Phone: (301) 975-6228
Email: taner@seas.upenn.edu

DOE Program Manager: Dr. Thiyaga P. Thiyagarajan
Phone: (301) 903-9706
Email: P.Thiyagarajan@science.doe.gov

Objectives

- Use neutron scattering methods along with first-principles computation to achieve fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen/methane and carbon capture in a wide spectrum of candidate materials.
- Study the effect of scaffolding, nanosizing, doping of the candidate materials on their hydrogen storage and dynamics properties.
- Provide timely feedback and guidance from theory to de novo materials design and targeted syntheses throughout the DOE programs.

Technical Barriers

- Currently there is no hydrogen storage materials which can be produced economically perform reversibly and reliably, and meet long-term storage targets e.g. reversible gravimetric capacity 6 wt% or better at practical temperatures and pressures.
- The main obstacles in hydrogen storage are slow kinetics, poor reversibility and high dehydrogenation temperatures for the chemical hydrides; and very low desorption temperatures/energies for the physisorption materials (metal-organic frameworks [MOFs], porous carbons).
- Carbon capture suffers from similar problems where the current technology is based on absorption in amine-based solvents which has limited reversibility and high regeneration cost. The solid-absorbers such as MOFs are either not stable against real flue-gas conditions and/or do not have large enough CO₂ capture (i.e. working) capacity to be practical and cost effective.

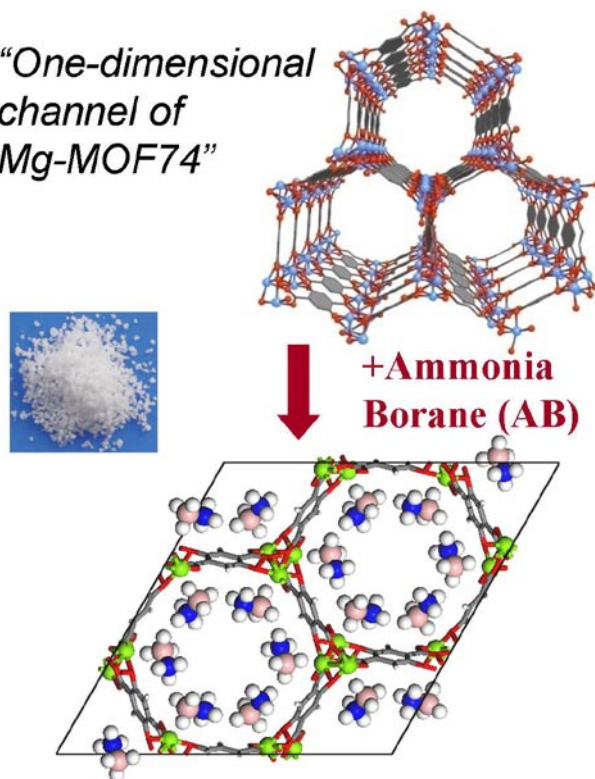
Abstract

Onboard hydrogen storage in fuel cell-powered vehicles is a major component of the national need to achieve energy independence and protect the environment. Fundamental breakthrough discoveries in materials science will be required to achieve light-weight, low-volume, safe, economical and recyclable storage technology. The goals of this proposal are a) to achieve fundamental microscopic understanding of how molecular hydrogen interacts chemically, structurally and energetically with novel storage materials; then b) use this understanding to predict and create nanoscale entities with precisely tuned hydrogen binding energies, which can c) be embedded as guests in nanoscale host scaffolds with large surface area to optimize hydrogen capacity, charge and discharge kinetics. This will be achieved by combining broad-based *ab initio* theory and computer modeling with novel materials synthesis and wide-ranging neutron scattering experimental studies.

Progress Report

We are currently working on many research avenues along the lines discussed in our original proposal. Below we briefly discuss some selected recent results.

“One-dimensional channel of Mg-MOF74”



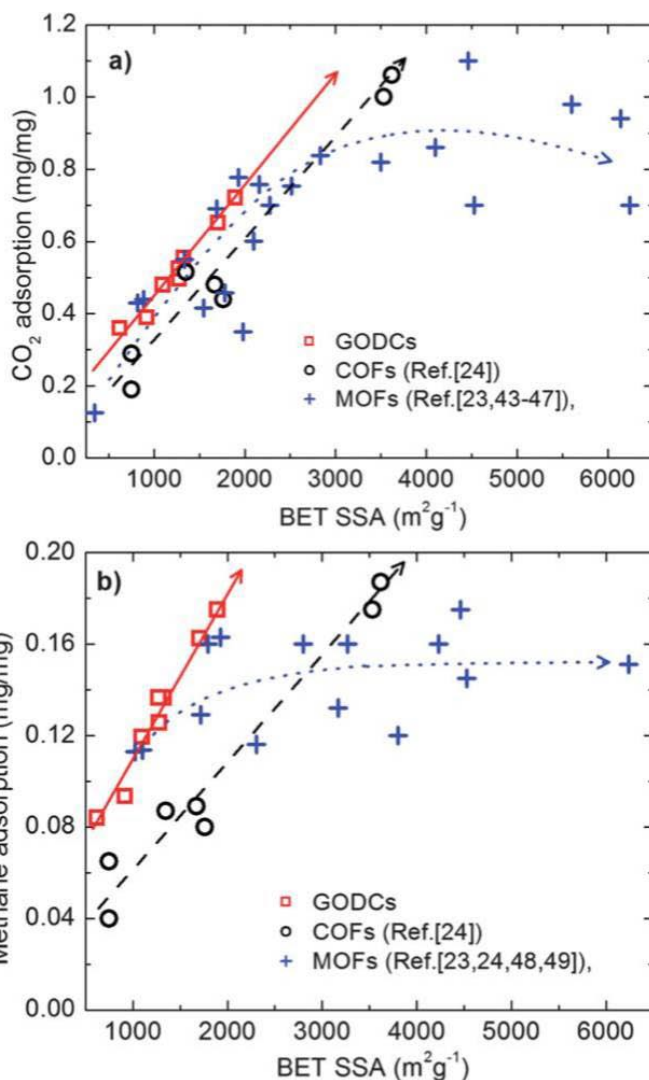
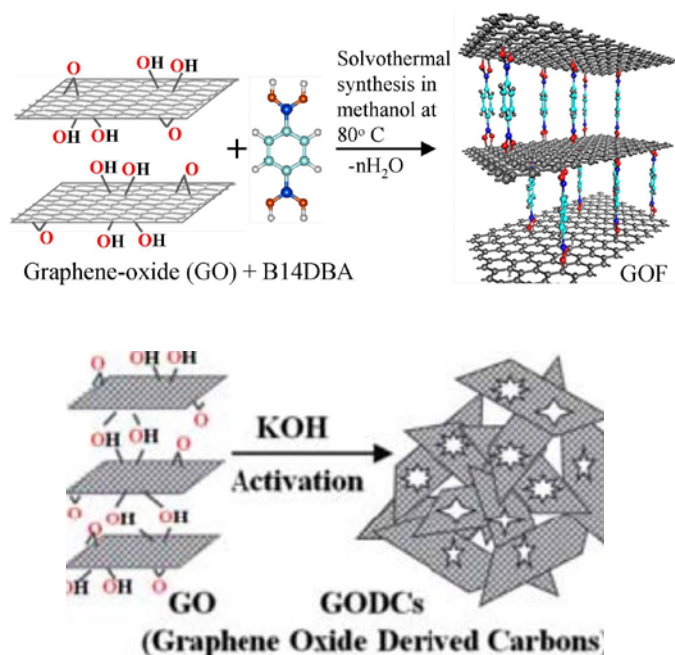
Clean and Fast Hydrogen Release from Nano-Confined AB-MOF Hybrid System

Ammonia borane (AB) has recently received much attention because of its satisfactory air stability, relatively low molecular mass and remarkably high energy storage densities (19.6 wt% and 140 g/L, respectively). However, the direct use of pristine AB as a hydrogen energy carrier in onboard/fuel cell applications is prevented by its very slow dehydrogenation kinetics below 100°C and the concurrent release of detrimental volatile by-products such as ammonia, borazine and diborane. In this study [8,9], we find that the nanoconfinement of AB molecules within the one-dimensional pores of Mg-MOF-74 could be an ideal system for delivering fast and clean hydrogen for fuel cell applications. We show that nanoconfined AB/MOF system improves the dehydrogenation kinetics significantly at temperatures <100°C. More importantly, the AB-Mg-MOF-74 system offers clean hydrogen delivery by suppressing the detrimental byproducts of ammonia, borazine, and diborane, thus putting us one step closer for using AB as hydrogen carrier for fuel cell applications.

Graphene Oxide Derived Carbons (GODCs): High-Surface Area NanoPorous Materials for Hydrogen Storage and Carbon Capture

Even though there has been extensive research on gas adsorption properties of various carbon materials based on activated carbon and nanotubes, there has been little work done on the gas adsorption properties of graphite oxide (GO). In this study, we show that one-and-a-half-century-old graphite oxide can be easily turned into a potentially

useful gas storage material. In order to create high-surface nanoporous materials from GO, we used two different approaches. In the first approach [10,5], we have successfully synthesized graphene-oxide framework materials (GOFs) by interlinking GO layers by diboronic acids. The resulting GOF materials have well defined pore size and Brunauer-Emmett-Teller surface area up to 500 m²/g with twice larger heat of adsorption of H₂ and CO₂ than those found in other physisorption materials such as MOF5. In the second approach [3], we synthesized a range of high surface area GO derived carbons (GODC) by chemical activation with potassium hydroxide and studied their applications toward H₂, CO₂, and CH₄ gas storage. We obtain largely increased surface areas up to nearly 1,900 m²/g for GODC samples from 10 m²/g for initial GO. A detailed experimental study of high pressure excess sorption isotherms on GODCs reveal an increase in both CO₂ and CH₄ storage capacities compared to other systems such as MOFs, zeolitic imidazolate frameworks, and COFs (see figure). On comparing with respect to the surface area below 2,000 m²/g, it is clear that



none of the MOFs surpass CO₂ and methane adsorption capacities of the GODCs. It is important for the potential adsorbents to be stable in the presence of flue gases in which the most of MOFs do not survive. In this regard, the new GODC materials with the rigid pores, good chemical resistance, high surface areas and tuneable pore volume could play a promising role as high pressure adsorbents. These results clearly demonstrate that GODCs are very promising solid adsorbents for gas adsorption applications due to their easy synthesis, tunable pore size/volume, high chemical stability and low cost production.

Efficient Carbon Capture in Metal-Organics Frameworks

Investigations of the application of MOFs to adsorptive carbon capture have focused on their appreciable storage capacities but fail to address the more pertinent issue of how MOFs perform under common industrial separation processes that are at the heart of carbon capture. Typical processes rely on swing adsorption and are limited to relatively low CO₂ partial pressures such that the total pore volume and the surface area are under-utilized. Here, we investigate the performance of a number of MOFs with particular focus on their behavior at the low pressures commonly used in swing adsorption. This comparison clearly shows that it is the process that determines which MOF is optimal rather than there being one best MOF, though MOFs that possess enhanced binding at open metal sites generally perform better than those with high surface area. In particular, using neutron scattering we unveiled the mechanism of carbon capture and found that MOFs that possess coordinatively unsaturated metal centers offer as much as 9 mmol g⁻¹ swing capacity under certain conditions. This work [4] will be an important guideline for deciding the best pair of carbon capture process and MOF material for optimum carbon capture.

Future Directions

We will focus our efforts on AB-hybrid systems and try to regenerate MOFs after AB is decomposed, which will make the hydrogen storage reversible. We will perform more work on nanoporous carbon materials derived from GO and MOFs, functionalize them such as B and N doping to tune their hydrogen storage and carbon capture properties.

Recent Publications acknowledging the DOE BES grant

1. *Direct Observation of Activated Hydrogen Binding to a Supported Organometallic Compound at Room Temperature*, J.M. Simmons, T. Yildirim, A. Hamaed, D.M. Antonelli, M.I. Webb, and C.J. Walsby, *Chem. Eur. J.* **18**, 4170 (2012).

2. *Metal hydrazinoborane LiN₂H₃BH₃ and LiN₂H₃BH₃•2N₂H₃BH₃: Crystal structures and high-extent dehydrogenation*, H. Wu, W. Zhou, F. Pinkerton, T. Udovic, T. Yildirim and J. Rush, *Energy Environ. Sci.*, DOI: 10.1039/C2EE21508J, Communication (2012)

3. *Graphene oxide derived carbons (GODCs): synthesis and gas adsorption properties*, G. Srinivas, J. Burress and T. Yildirim, *Energy Environ. Sci.* **5**, 6453-6459 (2012, commun.)

4. *Carbon capture in metal-organic frameworks—a comparative study*, J.M. Simmons, H. Wu, W. Zhou and T. Yildirim, *Energy Environ. Sci.* **4**, 2177-2185 (2011).

5. *Porous graphene oxide frameworks: Synthesis and gas sorption properties*, G. Srinivas, J.W. Burress, J. Ford and T. Yildirim, *J. Mater. Chem.* **21**, 11323-11329 (2011).

6. *Sodium magnesium amidoborane: the first mixed-metal amidoborane*, H. Wu, W. Zhou, F.E. Pinkerton, M.S. Meyer, Q. Yao, S. Gadipelli, T.J. Udovic, T. Yildirim and J.J. Rush, *Chem. Commun.* **47**, 4102-4104 (2011).

7. *“A highly practical route for large-area, single layer graphene from liquid carbon sources such as benzene and methanol”*, G. Srinivas, I. Calizo, J. Ford, G. Cheng, A.H. Walker, and Taner Yildirim, *J. Mater. Chem.* **21**, 16057-16065 (2011).

8. *Zn-MOF assisted dehydrogenation of ammonia borane: Enhanced kinetics and clean hydrogen generation*, G. Srinivas, J. Ford, Wei Zhou, and Taner Yildirim, *Int. Journal of Hydrogen Energy*, doi:10.1016/j.ijhydene.2011.04.008 (2011).

9. *Nanoconfinement and catalytic dehydrogenation of ammonia borane by magnesium-metal-organic-framework-74*, G. Srinivas, J. Ford, W. Zhou, H. Wu, T.J. Udovic, and Taner Yildirim, *Chem. Eur. J.* **17**, doi:10.1002/chem.201100090 (2011)

10. *Graphene-Oxide-Framework (GOF) Materials; Theoretical Predictions and Experimental Results*, J. Burress, G. Srinivas, J.M. Simmons, J. Ford, W. Zhou, Taner Yildirim, *Angew. Chem. Int. Ed.*, **49**, 8902-8904 (2010).

11. *Structural stability and elastic properties of prototypical covalent organic frameworks*, W. Zhou, H. Wu, Taner Yildirim, *Chem. Phys. Lett.* **499**, 103-107 (2010).

12. *A new family of metal borohydride ammonia borane complexes: Synthesis, structures, and hydrogen storage properties*, H. Wu, W. Zhou, F.E. Pinkerton, M.S. Meyer, G. Srinivas, Taner Yildirim, T.J. Udovic, *J. Mat. Chem.* **20**, 6550 (2010).

13. *Adsorption Sites and Binding Nature of CO₂ in Prototypical Metal-Organic Frameworks: A Combined Neutron Diffraction and First-Principles Study*, H. Wu, J. M. Simmons, G. Srinivas, W. Zhou, and Taner Yildirim *J. Phys. Chem. Lett.* **1**, 1946 (2010).

14. *Metal-Organic Frameworks with Exceptionally High Methane Uptake: Where and How is Methane Stored?*, H. Wu, J.M. Simmons, Y. Liu, C.M. Brown, X.-S. Wang, S. Ma, V.K. Peterson, P.D. Southon, C.J. Kepert, H.-C. Zhou, T. Yildirim, and W. Zhou, *Chem. Eur. J.*, **16**, 5205–5214 (2010).

15. *Alkali and alkaline-earth metal dodecahydro-closo-dodecaborates: Probing structural variations via neutron vibrational spectroscopy*, N. Verdal, W. Zhou, V. Stavila, J.-H. Her, M. Yousufuddin, T. Yildirim, and T.J. Udovic, *J. Alloys Comp.* (2010).

16. *Metal Amidoboranes*, Hui Wu, Wei Zhou, and Taner Yildirim, in *“Boron Hydrides, High Potential Hydrogen Storage Materials*, edited by Umit B. Demirci and Philippe Miele, Nova Publishers (2010).