

IV.C.4 Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

John E. Fischer (Primary Contact),
Yury Gogotsi (Drexel), Taner Yildirim (NIST)
Department of Materials Science and Engineering
University of Pennsylvania
3231 Walnut St.
Philadelphia, PA 19104-6272
Phone: (215) 898-6924; Fax: (215) 573-2128
E-mail: fischer@seas.upenn.edu

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

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Objectives

- Develop and demonstrate reversible hydrogen storage in carbide-derived carbons (CDCs). Determine the optimum pore size for hydrogen storage.
- Design a CDC that meets DOE performance targets and commercialize it.

Technical Barriers

This project addresses the following technical barriers from the Storage section the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

- 2 kWh/kg (6 wt%) gravimetric capacity
- 1.5 kWh/L volumetric capacity
- Reversibility and reproducibility

Accomplishments

Our accomplishments for the first 9 months of FY 2006 are as follows:

- Synthesized and tested 40 CDC porous carbon cryosorbents.
- Established correlation between pore size distributions (PSD) derived from gas sorption and small-angle x-ray scattering (SAXS).
- Designed and built an automated Sieverts apparatus.
- Discovered annealing in hydrogen increases the volume of small pores.
- Established correlation between cryosorption efficiency and the volume of pores with diameters <1 nm.
- Discovered capacity enhancements based on increasing the heat of adsorption, by adding Ti, Ni, etc., to the carbon skeleton.

Introduction

One possible route to practical on-board hydrogen storage in fuel cell vehicles is the use of solid state cryosorbents in which the amount of hydrogen exceeds that in the pressurized gas, or even liquid, under appropriate thermodynamic conditions. The drawbacks with existing cryosorbents are the need for a huge volume to achieve acceptable range, and/or the requirement for very high pressures and/or low temperatures to achieve the same goal. In this project we attempt to advance the state-of-the-art by designing, making and measuring a porous carbon cryosorbent which overcomes these limitations by a) providing an adequate volume of small pores which act as mini-reservoirs for hydrogen, and b) to fine tune the hydrogen-carbon interactions to provide stable, reversible and controllable hydrogen storage under practical operating conditions of driving and refueling.

We have made significant progress towards this goal by synthesizing gram quantities of the most promising CDCs to enable round-robin testing evaluation, setting up theoretical models to predict new candidates, and modifying the synthesis (additives, catalysts) in response to theoretical results for enhanced capacity. We seek to understand in detail, from theory and experiment, the nature of the hydrogen-carbon interaction by performing first-principles molecular dynamics simulations to guide improved storage dynamics. The performance targets will be achieved by a combination of solid

state synthesis, macro and microscopic materials characterization, first-principles theory and high-level computer simulations. The full parameter space of synthesis variables will be surveyed, with guidance from theory, in order to identify CDCs with maximum storage performance. Scale-up from tube furnace to fluidized bed will be accompanied by a search for industrial partners.

Approach

We will synthesize a large number of CDCs and optimize them for hydrogen storage. The most important variables are chlorination temperature and choice of starting carbide (binary, ternary, alloy, etc.). The Drexel team led by Prof. Gogotsi is carrying out most of the materials synthesis, Bruner, Emmett and Teller (BET) surface area and Density Functional Theory (DFT) pore size distribution measurements, low pressure hydrogen storage measurements, Raman spectroscopy, and transmission electron microscopy (TEM) characterization. The Penn team led by Prof. Fischer uses a large number of experimental techniques such as SAXS, x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS) and calorimetric sorption to characterize local structure, binding, and sorption properties of CDCs. The NIST group led by Dr. Yildirim will utilize neutron scattering and high-pressure hydrogen absorption experiments in combination with first-principles, molecular dynamics and phase-diagram computational techniques to guide and interpret the experiments.

Once the basic survey is complete, we will study the effect of catalysts such as Pt, Ti, alkali metals, etc., on the storage capacity. Scattered reports in the literature suggest that such additives may maximize the storage capacity of CDC. In parallel, we will scale up the synthesis of CDC and try different routes to reduce the material cost. A closed-cycle and environmentally friendly process using fluidized bed reactors will be designed in collaboration with industry.

Results

Importance of Pore Size for Optimizing Hydrogen Storage Capacity

A systematic study of more than 30 CDCs shows that subnanometer pores are more efficient than larger ones for H_2 adsorption, especially using face-centered cubic precursors such as TiC and ZrC. Figure 1 shows the gravimetric capacity normalized to total BET surface area, versus the average pore size determined from non-local density functional theory (NLDFT). Data for many CDCs lie within the triangular region defined by the dashed lines, which extrapolate to 2.6% per 1000 m^2 of area. Promising materials are found in the upper left,

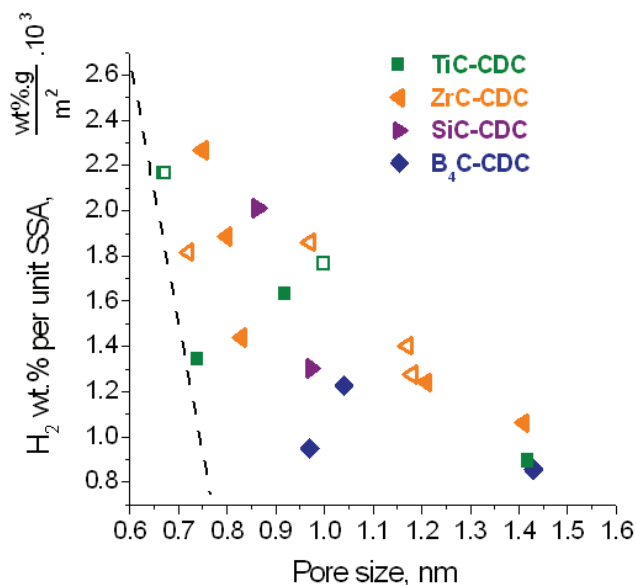


FIGURE 1. Correlation between hydrogen capacity and volume of subnanometer pores. Open symbols denote hydrogen annealing after synthesis.

rejects on the lower right. The capacity of a hypothetical CDC with 2600 m^2/g specific surface area (SSA) of subnanometer porosity would satisfy the DOE short term 6% requirement at 1 atm. and 77 K. Annealing in hydrogen after synthesis (open symbols) increases the volume of small pores available for storage by removing residual Cl_2 . The significance of this result for the EERE program is that it provides a basis for rational design of optimum cryosorbers for hydrogen.

Heats of Adsorption: CDC vs. other Cryosorbers

Recent calculations [1] show that the heat of adsorption of hydrogen for an ideal hydrogen cryosorber is 15 kJ/mole if both the delivery and storage is to occur at room temperature. This value is considerably higher than the average heat of adsorption of hydrogen on activated carbons and carbon nanotubes (CNTs) (5-6.5 kJ/mol) as well as on metal organic framework (MOF) (0-7 kJ/mol). Our systematic experimental investigation of a large number of CDCs with controlled pore size distributions and SSA show how smaller pores increase both the heat of adsorption and the total volume of adsorbed H_2 . It has been demonstrated that increasing the average heat of H_2 adsorption above 6.6 kJ/mol substantially enhances uptake at 1 atm and 77 K. The heats of adsorption up to 11 kJ/mol exceed values reported for MOF compounds and CNTs (cf., Figure 2). Small pores increase the interaction with H_2 (higher heat of adsorption) and thus result in higher coverage of the sorbent surface. The significance of this result is that CDCs demonstrate stronger interaction with hydrogen

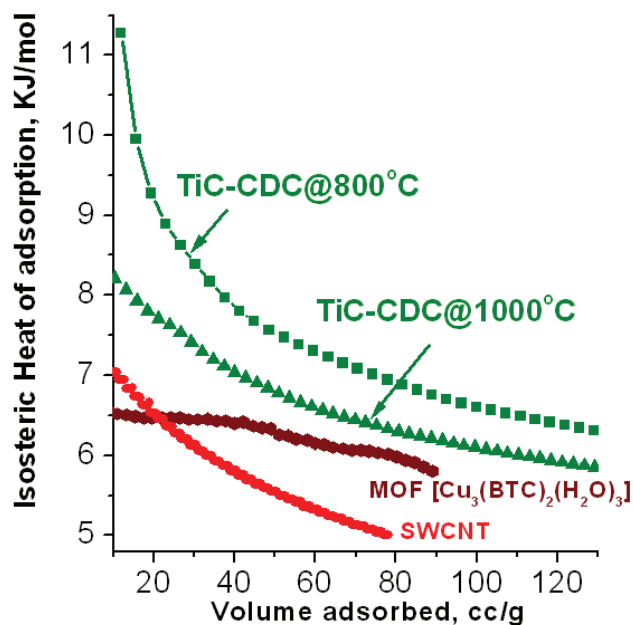


FIGURE 2. Comparison of CDC isosteric heats of adsorption with a MOF compound and with single-wall carbon nanotubes. The CDC values are significantly higher, indicating stronger interaction between hydrogen and the pore walls.

than CNTs or MOFs, and are thus better suited to high temperature, low pressure applications.

Nature of the Hydrogen Interaction and Effects of Transition Metals on Carbon-Based Nanoscale Cryosorbers

Recently we predicted [2] that Ti-decorated carbon nanotubes can adsorb up to 8 wt % hydrogen at ambient conditions. Here we report that a similar phenomenon occurs in light transition-metal decorated C_{60} . While Sc and Ti prefer the hexagon (*H*) sites with a binding energy of 2.1 eV, V and Cr prefer double-bond (*D*) sites with binding energies of 1.3 and 0.8 eV, respectively. Heavier metals such as Mn, Fe, and Co do not bond on C_{60} . Once the metals are adsorbed on C_{60} , each can bind up to four hydrogen molecules with an average binding energy of 0.3–0.5 eV/ H_2 . At high metal coverage, one C_{60} molecule accommodates six *D*-site and eight *H*-site metals (total 52), corresponding to 7.5 wt%. The predicted geometries for Ti-decorated C_{60} are shown in Figure 3. The significance of these results is that similar enhancements in capacity and heat of adsorption can be expected by light transition metal doping of our porous CDCs, as described below.

Conclusions and Future Directions

Accomplishments in 2006 lead to the conclusion that CDCs outperform previous cryosorbers based

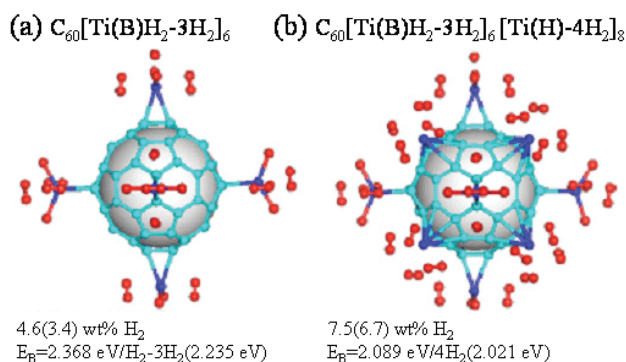


FIGURE 3. Two hypothetical Ti-coated C_{60} systems with high density *H* coverage. They correspond to 4.3 wt% and 7.5 wt% *H* storage if all hydrogens can be released, and to 3.4 wt% and 6.7 wt% *H* storage if only molecularly adsorbed hydrogens can be released. We expect similar results from Ti-decorated pores in CDC.

on carbon, and provide realistic alternatives to other candidate material families for onboard hydrogen storage. Their primary advantages are light weight, easy reversibility and low cost. The challenges are to increase gravimetric and volumetric capacity to achieve DOE targets. These will be the focus of our future work.

We will address volumetric capacity for the first time, by making and studying compacts of CDC powders. We need to determine the limiting conditions for palletizing, beyond which we begin to lose *gravimetric* capacity by “crushing” the micropores. This should be relatively high, permitting a large degree of volume reduction.

Two separate approaches are being taken to enhance gravimetric capacity: chemical post-treatments and testing chlorination reactions on different precursor morphologies. We have tested two post-treatments so far: annealing in hydrogen, which was successful, and “activation” by high temperature CO_2 treatment, which was not. We have begun work with KOH activation, and will soon begin experiments with Ti doping as suggested by modeling results. We are also testing a novel activation chemistry which we are not ready to make public.

Ti-decorated C_{60} and single-walled carbon nanotubes (SWNTs) are closely related to CDC. Prompted by the theoretical results obtained on the computationally tractable *ordered* carbons, we hope to incorporate similar dopants in the amorphous carbon CDC micropores. Two approaches will be taken: incorporation of Ti after the CDC is synthesized, and retaining some Ti from Ti-containing precursors (TiC, Ti_3SiC_2) during the chlorination. Hydrogen uptake vs. Ti concentration will be measured, relying on prompt gamma activation analysis (PGAA) to accurately determine the Ti to C ratio. Ti-doped CDC should have several advantages over Ti/ C_{60} and Ti-SWNT. The open

surfaces of the latter nanostructures suggest that they may exhibit clustering of Ti during hydrogen cycling, which in turn would cause a gradual loss of storage capacity. We will study these and other practical issues using molecular dynamics simulations.

FY 2006 Publications

1. Molecular and Dissociative Adsorption of Multiple Hydrogens on Titanium-decorated C60, T. Yildirim, J. Iniguez and S. Ciraci, *Phy. Rev Letters* (in press).
2. Normal Mode Analysis and First-Principles Molecular Dynamics Study of C60Ti_yH_x Clusters for Room Temperature Reversible Hydrogen Storage, J. Iniguez, W. Zhou and T. Yildirim (in preparation, 2006).
3. Titanium Carbide-Derived Nanoporous Carbon for Energy-Related Applications, R.K. Dash, G. Yushin, G. Laudisio, J. Chmiola, J. E. Fischer, Y. Gogotsi, *Carbon*, (in press).
4. Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium, T. Yildirim and S. Ciraci, *Phy. Rev Letters* **94**, 175501 (2005).
5. Design of Porous Carbon for Efficient Hydrogen Storage, G. Yushin, R.K. Dash, J. Jagiello, J. E. Fischer, Y. Gogotsi, *Adv. Funct. Mat.* (in press).
6. Carbide-Derived Carbons: A Comparative Study of Porosity Based on Small-Angle Scattering and Adsorption Isotherms, G. Laudisio, R.K. Dash, G. Yushin, J.P. Singer, Y. Gogotsi, J.E. Fischer, *Langmuir* (in press).

FY 2006 Presentations

1. From fundamental understanding to predicting new nanomaterials for high capacity hydrogen storage technologies, **T. Yildirim**, APS March Meeting, Baltimore 2006.
2. Carbide Derived Carbon Designed for Efficient Hydrogen Storage, **R.K. Dash**, G. Yushin, G. Laudisio, T. Yildirim, J. Jagiello, J.E. Fischer and Y. Gogotsi, Spring MRS Symposium, San Francisco, April 2006.
3. Combined Neutron Scattering and First-Principles Study of Novel Hydrogen Storage Materials, **T. Yildirim**, Spring MRS Symposium, San Francisco, April 2006.
4. Tailored nanoscale porosity in carbide-derived carbons optimized for hydrogen storage, **John E. Fischer**, Giovanna Laudisio, Jonathan P. Singer, Ranjan K. Dash, Gleb Yushin, Yury Gogotsi, Taner Yildirim, E-MRS Symposium E, Hydrogen Storage Materials, Nice, France, May 2006.
5. **John E. Fischer**, presentation regarding the overall project status given at the DOE Annual Merit Review Meeting (May 2006).

6. Neutron Scattering and First-Principles Characterization of Novel Hydrogen Storage Materials, **T. Yildirim**, American Conference on Neutron Scattering, St. Charles, IL, June 18-22, 2006.
7. Magic Role of Ti in Novel Hydrogen Storage Materials, **T. Yildirim**, the XV International Materials Research Congress (IMRC), Cancún, August 20–24, 2006.
8. Tailored nanoscale porosity in carbide-derived carbons: optimization for high capacity hydrogen storage, **Yury Gogotsi** et al., UCSB Conference on Hydrogen Storage (sponsored by DOE) August 2006.
9. Tailored nanoscale porosity in carbide-derived carbons: optimization for high capacity hydrogen storage, **John E. Fischer**, invited talk at *MH2006* (Metal-Hydrogen interactions), Maui (October 1–4, 2006).
10. Hydrogen and Methane in MOF - Isotherms, Heat of Absorptions and INS Data, **Wei Zhou** and Taner Yildirim, *MH2006* (Metal-Hydrogen interactions), Maui (October 1–4, 2006).
11. Characterization of Carbide Derived Carbons (CDC) structure and its effect on hydrogen storage, **J. P. Singer**, G. Laudisio, A. B. Seletsky, R. K. Dash, G. Yushin, W. Zhou, T. Yildirim, Y. Gogotsi, J.E. Fischer, submitted to the MRS Fall Meeting, Symposium Z: Hydrogen Storage Technologies, Boston, November 27–December 1, 2006.
12. Carbide-derived carbons: effect of pore size on hydrogen uptake and heat of adsorption, **Gleb Yushin**, Ranjan K. Dash, Daniel Vriehof, Yury Gogotsi, Taner Yildirim, Giovanna Laudisio, Jonathan P. Singer, John E. Fischer, submitted to the MRS Fall Meeting, Symposium Z: Hydrogen Storage Technologies, Boston, November 27–December 1, 2006.

References

1. S.K. Bhatia and A.L. Myers, *Langmuir*, **2006**, *22*, 1688-1700.
2. T. Yildirim and S. Ciraci, *Phys. Rev. Lett.* **94**, 175501 (2005).

Awards

Nanotech Briefs “Nano 50” award in the *Technology* category to Drexel University for development of Carbide-Derived Carbons. *Nanotech Briefs* magazine is the monthly digital publication from the publishers of NASA Tech Briefs. “Nano 50” recognizes the top 50 technologies, products, and innovators that have significantly impacted, or are expected to impact, the state of the art in nanotechnology.