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

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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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

Technical Targets

This project is conducting fundamental studies of CDCs for onboard hydrogen storage. Insights gained from these will be applied to the optimization, design, synthesis and scale-up of hydrogen storage materials that meet DOE 2010 targets: gravimetric capacity 2 kWh/kg; volumetric capacity 1.5 kWh/liter and system cost: $4/kWh net.

Accomplishments

- Developed post-processing purification methods involving heat treatment in hydrogen or ammonia which remove unreacted precursor material and improve gravimetric capacity.
- Established a database of more than 60 distinct CDC materials to date, synthesized and fully characterized with respect to pore surface properties and hydrogen storage performance.
- Showed convincingly that pores <1 nm dominate the storage capacity; larger ones are less effective and mostly degrade the volumetric capacity. Strong departures from linear dependence of capacity on total surface area are observed both at 1 atm and 40 atm.
- Using nanodiamond as a surrogate, showed that "pore" surface treatment e.g. amination leads to significant enhancement in storage capacity, primarily by increasing the heat of adsorption since the pore volume and surface area are unchanged.
- Found that activation of CDCs by KOH or CO_2 increases the gravimetric capacity by as much as 30%, increasing the number of candidates for further optimization.
- Addressed the issue of volumetric capacity of materials processed as powders, compacting them by rolling peels or pressing pellets; the best value to date is 29 g H_2/liter.

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Introduction

Carbon supports a large number of novel structures with large surface area, e.g., activated carbon, fullerenes, carbon nanotubes, etc. An isolated flat graphene sheet has a specific surface area (SSA) of 2,600 m^2/gram, but the enthalpy of *physisorption* is so low that reversible hydrogen storage would require a combination of

low temperature and high pressure. First-principles calculations indicate that *chemisorption* on pores with small radii of curvature is possible, but reversibility of sorption/desorption is doubtful and would require high temperature operation to liberate hydrogen.

Thus our agenda for achieving practical carbon-based storage materials includes the following elements: a) discover materials with tunable and large pore volume, total surface area and optimized pore size and shape to take maximum advantage of C-H$_2$ interactions without introducing wasted volume; b) chemical treatments of the internal pore surface to increase binding enthalpy and facilitate operation near 300 K; and/or c) introduce small concentrations of appropriate metal dopants to achieve the same purpose *via* tailored orbital hybridization [1].

Approach

An excellent material family for this agenda is nanoporous carbide-derived carbon, or CDC, prepared by selective etching of crystalline carbides with chlorine gas in the range 300-1,200°C. Because the rigid metal carbide lattice is used as a template and the metal is extracted layer-by-layer, atomic-level control can be achieved in the synthesis process and the carbon structure can be templated by the carbide structure. We first confirmed experimentally that, relative to well-known activated carbons, CDC's indeed possess many advantages for hydrogen storage, such as narrow, zeolite-like pore size distributions (PSD) tunable with better than 0.05 nm sensitivity in the range ~0.5 to ~1.5 nm [2], SSA up to 2,000 m^2/g [3], and ~80% open pore volume [2]. With this point of departure we designed a series of systematic studies along several different directions, targeting increases in SSA, optimization of PSD and pore size, and if possible enhancement of the enthalpy of adsorption on pore surfaces.

Results

Gravimetric Capacity: Hydrogen storage measurements on peels formed from powdered CDCs mixed with 3–5 wt% fluropolymer binder were conducted. Polymer interactions with adsorption sites were explored by examining CDCs derived from different precursors. The observed trends in loss of gravimetric capacity suggest that the detrimental effect of the polymer is greatest for large (>1.5 nm) pores and small (<1.5 nm) particle sizes. Further densification was realized by palletizing stacks of peels. Our best-performing CDC sample displayed excess and total volumetric capacities of 0.021 and 29 g H$_2$/L, respectively at 77 K and 4 MPa hydrogen pressure. Figure 1 presents the results for TiC-derived CDCs. These show increasing loss of gravimetric capacity with increasing chlorination temperature. TiC CDCs have
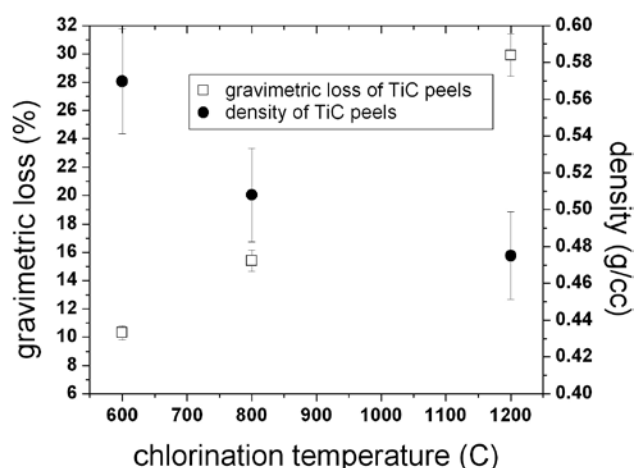

FIGURE 1. Percent loss of gravimetric capacity by forming a peel from powdered TiC-CDC plus fluropolymer binder (left axis), and peel density, both vs. chlorination temperature.

average pore sizes that are highly correlated to their chlorination temperature [4], and since all TiC samples were prepared from the same batch of precursor powder, other traits can be taken as comparable.

Activation of CDCs: The effects of (so-called) physical activation were studied using air and CO$_2$; chemical activation was represented by KOH. Air proved unsatisfactory because despite large increases in SSA, little or no improvement in storage capacity was obtained. We conclude that strong oxidizers lead to large pores which are not as effective as small ones (< 1.5 nm) – see below.

Carbon dioxide, a mild oxidizer, was used to activate TiC-600°C. Sorption data showed that SSA, pore volume and micropore volume were all significantly increased. Systematic studies revealed that the optimal conditions for high micropore volume is a compromise between activation time, temperature and burn-off. For example, micropore volume at 950°C is smaller than that of the pristine CDC, but the larger SSA and pore volume counterbalance this small value. As the porosity increases, a larger excess hydrogen capacity is observed, as shown in Figure 2. The largest capacity is obtained for samples activated at 950 and 875°C for 2 hours and 8 hours, respectively. Similar promising results were obtained with KOH, tested on both TiC- and SiC-derived CDCs.

Importance of Small Pores in High Pressure Storage: In Figure 3 we collect 77 K, 40 atm storage data for a wide variety of CDCs and other porous carbons. If the capacity depended only on total surface area SSA, the data would all lie on the central short-dashed line (Chahine rule). Instead, the data show a large range of over and underperformers, strongly suggesting that the details of the pore size and structure are equally important.
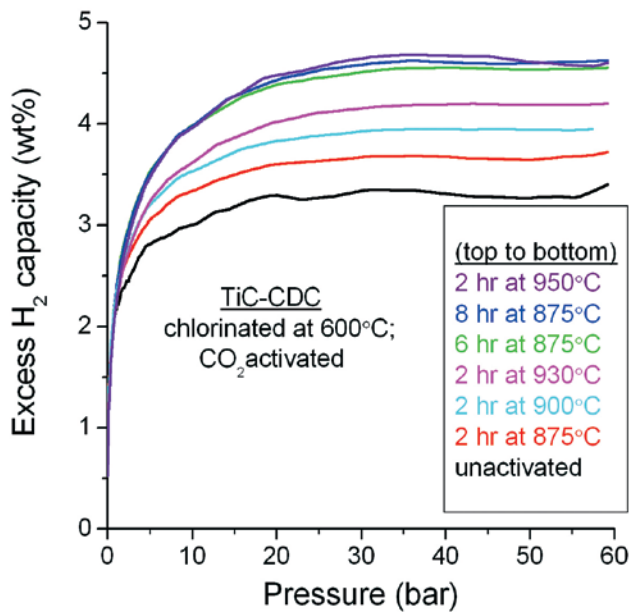
FIGURE 2. Pressure-dependent 77 K isotherm (Sieverts measurement) excess gravimetric capacities of TiC-CDCs chlorinated at 600°C, purified by hydrogen annealing at 600°C, and activated for various times and temperatures in CO_2. Bottom curve is for the un-activated control sample. Maximum improvement of ~50% is achieved for the three topmost time-temperature conditions in the legend.
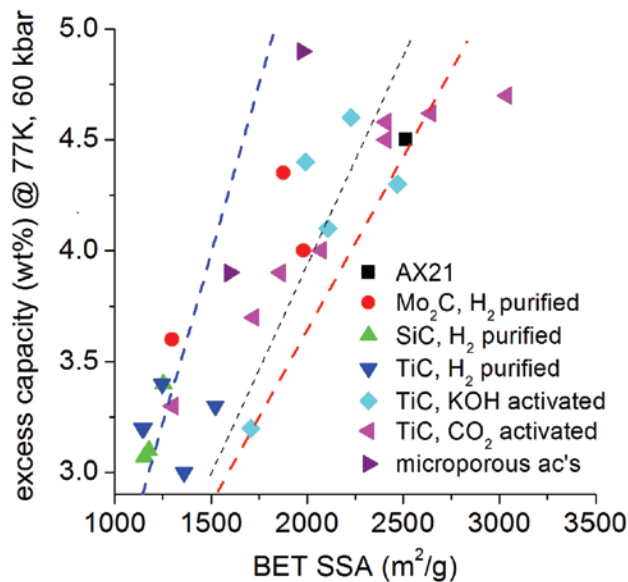
A clear and direct dependence of storage capacity on pore size is obtained by plotting hydrogen storage normalized to SSA vs. pore size, as was done for 1 atm storage. Figure 4 shows the results. The smallest pores provide the greatest contribution to total capacity, since the carbon-hydrogen interaction due to the overlap of the interaction potential fields from the interior pore surface will thus be enhanced. Furthermore, materials with monodisperse smaller pores have higher SSA for a given pore volume. This means that hydrogen storage is dominated by small pores and thus not directly connected to total SSA. Even at high pressure, H_2-H_2 interactions inside large pores are not strong enough for such pores to contribute importantly to overall capacity. Since storage occurs predominantly on the pore surfaces, the interior volume of large pores is essentially wasted and merely degrades the volumetric capacity. Our data and conclusions are completely borne out by a new calculation from Cabria et al. [5] who show that the optimum slit pore width at 20 MPa hydrogen pressure remains well below 1 nm.
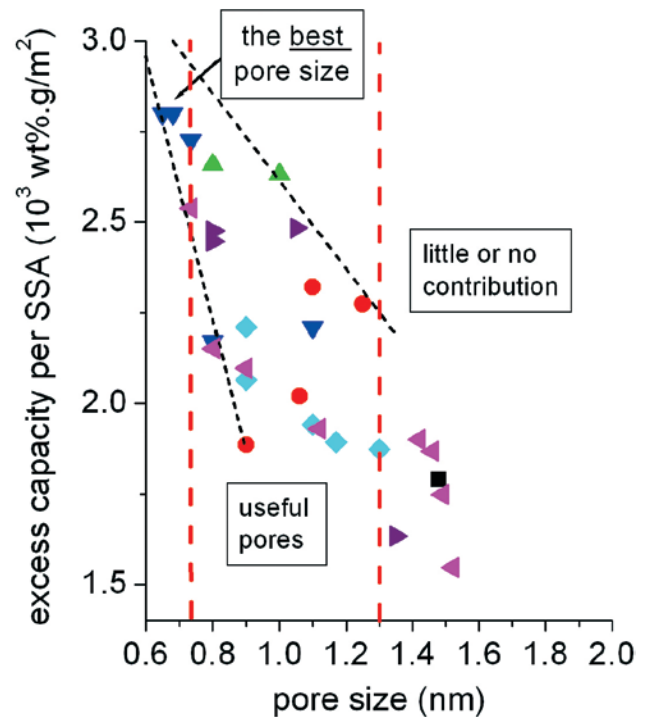

FIGURE 3. Excess gravimetric capacity (77 K, 40 atm) vs. specific surface area for a wide variety of CDCs and other amorphous microporous carbons. The central short-dashed line represents the Chahine rule: capacity (wt%) = 2 SSA (m^2/g), which assumes pores of all sizes contribute equally to hydrogen storage. The long dashed lines demarcate the overperformers and underperformers, and are drawn to approximately include the point (0,0). Overperformers contain larger fraction of pores <1 nm in their pore size distributions.

FIGURE 4. Excess gravimetric capacity (77 K, 40 atm) normalized to specific surface area, plotted as a function of average pore size, for a wide variety of CDCs and other amorphous microporous carbons. The widely scattered data points confirm that capacity is not simply related to total porosity, but rather that pores in the range <1 nm are much more effective at storing hydrogen than larger pores >1.2 nm.

Conclusions and Future Directions

- Purified CDCs subjected to chemical or physical activation equal or slightly exceed, gravimetric capacity of activated carbons.

- Large pores (d >1.5 nm) are less effective than small ones, both at high and low pressure.

- Spinoff startup Y-Carbon licensed to scale-up CDC manufacturing - $243,835 in hand.

- Determine atomic-level pore structure by neutron scattering and hybrid reverse Monte Carlo analysis (with Los Alamos National Laboratory and North Carolina State University).

- Apply surface treatments, especially amination, to CDC for enhanced binding.

- Study effect of sequential application of activation, surface treatment and/or doping.

Special Recognitions & Awards/Patents Issued

1. 11 patents filed by Y-Carbon: http://www.y-carbon. us. Relevant example: "Process for producing nanoporous carbide-derived carbon with large specific surface area", PCT/US2006/045154 (2006).

2. Yury Gogotsi elected fellow of the American Ceramic Society.

FY 2008 Publications/Presentations

1. "Desolvation of ions in subnanometer pores, its effect on capacitance and double-layer theory", J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Angewandte Chemie Int. Edition* 47 (18), 3392-3395 (2008).

2. "Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor", C. Largeot, C. Portet, J. Chmiola, P.L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* **130** (9), 2730-2731 (2008).

3. "Enhanced Volumetric Hydrogen Storage Capacity of Porous Carbon Powders by Forming Peels or Pellets", J. P. Singer, A. Mayergoyz, C. Portet, E. Schneider, Y. Gogotsi and J. E. Fischer, Mesoporous and Microporous Materials (in press).

4. "Carbide Derived Carbon and Templated Carbons", T. Kyotani, J. Chmiola, Y. Gogotsi, in *Carbons and Composites for Electrochemical Energy Storage Systems*, edited by F. Beguin and E. Frackowiak, CRC Press/Taylor and Francis, (2008) in press.

5. "Molybdenum carbide derived carbon for hydrogen storage", Hyun Seok Kim, Jonathan P. Singer, Yury Gogotsi and John E. Fischer, Mesoporous and Microporous Materials (submitted).

6. "Importance of Pore Size in High Pressure Hydrogen Storage by Carbide Derived Carbons", Y. Gogotsi, C. Portet, S. Osswald, T. Yildirim, G. Laudisio and J. E. Fischer, *Chem. Comm*. (submitted).

7. "Hybrid reverse Monte Carlo simulations of nanoporous carbons", J. Palmer, S. Jain, K. Gubbins, N. Cohaut, J. E. Fischer and Y. Gogotsi, *Proceedings of the 8th International Symposium on the Characterisation of Porous Solids*, (2008).

8. "Carbide-Derived Carbons for Energy-Related Applications", Y. Gogotsi, *University of Connecticut, School of Engineering*, February 28, 2008.

9. "Nanostructured Carbons and Carbon-Based Nanocomposites for Energy Related Application", G. Yushin, *American Chemical Society 235th National Meeting*, New Orleans, Louisiana, April 2008 (invited).

10. "Progress in Carbide-Derived Carbons for Energy Related Applications", Y. Gogotsi, keynote address at *Carbon for Energy Storage and Environment Protection Conference*, Sept. 2-6, Krakow, Poland.

11. "Porous Carbons for Hydrogen Storage: Physics, Chemistry and Prospects", J. E. Fischer, G*eorgetown University*, Oct. 9, 2008.

References

1. "*Metal Dihydrogen and Bond Complexes–Structure, Theory and Reactivity*", edited by G. J. Kubas _Kluwer Academic/Plenum, NY (2001).

2. "Nanoporous carbide-derived carbons with tuneable pore size", Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J. E. Fischer, B. Ye, H. Foley and M. Barsoum, *Nature Materials* **2,** 591 (2003).

3. "Synthesis, structure and porosity analysis of microporous and mesoporous carbon derived from zirconium carbide", R.K. Dash, G. Yushin, Y. Gogotsi, *Microporous and Mesoporous Materials* **86** 50–57 (2005).

4. "Carbide-Derived Carbons: Effect of Pore Size on Hydrogen Uptake and Heat of Adsorption", G. Yushin, R. K. Dash, J. Jagiello, J. E. Fischer and Y. Gogotsi, *Adv. Funct. Mater.* **16,** 2288–2293 (2006).

5. "The optimum average nanopore size for hydrogen storage in carbon nanoporous materials", I. Cabria, M. J. Lopez and J. A. Alonso, *Carbon* **45,** 2649–2658 (2007).