# VI.C.2 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 (CDC) with tunable nanoporosity.
- Determine the optimum pore size for hydrogen storage using experiment and theory.
- Design a CDC-based hydrogen storage material that meets 2010 DOE performance targets and commercialize it.

## Technical Barriers

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

- B. Weight and Volume
- C. Efficiency
- M. Hydrogen Capacity and Reversibility.
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption.

## Technical Targets

The main focus will be on meeting the following specific targets:

- By 2010, develop and verify on-board hydrogen storage materials achieving storage system targets of 2 kWh/kg (6 wt%), 1.5 kWh/L, fill time of 3 minutes for 5-kg of hydrogen, and $4/kWh.

**Table 1.** On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)

| Storage Parameter | Units | 2010 System Target | FY 2005 CDC materials |
|---|---|---|---|
| Specific Energy | wt. % H2 | 6 wt.% | 3.5 wt% at 77K, 8 atm |
| Volumetric Energy Capacity | kWh/L | 1.5 | 0.83 kWh/L assuming $\rho$ = 0.98 g/cc |

## Approach

A new kind of nanoporous carbon with tunable pore size is being developed. Carbide-derived carbons (CDC) are expected to have a greater hydrogen storage capacity than all of the other carbons studied to date. The reason is that CDC pore size can be precisely tuned to match the appropriate molecular diameter, with a better than 0.5 Å accuracy in the range 5-15 Å, by optimizing the choice of precursor carbide and chlorination temperature. Specific surface area (SSA) of up to 2,000 $m^2/g$ and up to 80% open pore volume are readily achievable, and the materials are projected to be very cheap compared to e.g. nanotubes.

Key milestones (chronological):

- Synthesize gram quantities of most promising CDCs to enable round-robin testing evaluation (09/06).
- Set up theoretical models to predict new candidates (09/05).
- Modify synthesis (additives, catalysts) in response to theoretical results for enhanced capacity; achieve 4% (wt.) (09/06).
- Understand in detail, from theory and experiment, the nature of the hydrogen-carbon interaction (09/07).
- Perform first-principles molecular dynamics simulations to guide improved storage dynamics. (09/07).
- Achieve commercialization and scale-up; seek commercial partner. (09/08).

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.

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 Professor Gogotsi is carrying out most of the materials synthesis, basic Brunauer, Emmett and Teller (BET) surface measurements, Raman spectroscopy and transmission electron microscopy (TEM) characterization. The Penn team led by Professor Fischer uses a large number of experimental techniques such as small-angle X-ray scattering (SAXS), X-ray diffraction (XRD), energy-dispersive (X-ray) scattering (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.

## FY 2005 Accomplishments

High Capacity Storage in Porous CDC

Thermodynamic and kinetic parameters of the adsorption/desorption process were evaluated as a function of pore size and distribution for different CDCs with a Sieverts-type apparatus. High pressure measurements from 0 to 8 atm and 77K were also carried out to relate the loading/release of hydrogen to temperature and $H_2$ pressure with the ultimate aim of optimizing the hydrogen storage. The achieved gravimetric hydrogen uptake for CDCs is 3.5 wt% at 77K and 8 atm, about twice that of MOF-5 and several times higher than high-pressure carbon monoxide (HiPCo), a method for making single-walled carbon nanotube (SWCNT), or chemically modified SWCNT. Reproducibility is demonstrated by excellent agreement between storage values obtained from Quantachrome Autosorb-1 measurements performed independently in two laboratories. CDCs are produced by extraction of the metal (and metalloids) from carbide precursors in halogen atmosphere. The resulting material has high surface area and pore size tunable with sub-Angstrom accuracy determined by the crystal structure of the starting material and the choice of process parameters. The atomic-level control on porosity in CDC porous carbon offers the unique opportunity to carry out a systematic study of gas adsorption phenomena and to better understand hydrogen sorption in porous materials.

CDC synthesis is quite efficient, so large samples, 0.5 gram or greater, are available for isotherm and Sieverts measurements. In a round-robin test of reproducibility, we tested the gravimetric capacity of a prototype CDC using three different instruments in two different labs. Autosorb-1 has been in service at Drexel well before the current grant started. Nova is a similar instrument located at the manufacturer's plant. Quadrasorb was purchased for this project and has just been put into service. The excellent reproducibility is evidenced by the graph in Figure 1. Here the maximum hydrogen uptake of 300 mg/L at 1 atm corresponds to 2.5 wt%, within 20% of the highest storage capacity achieved so far at 1 atm in any material.

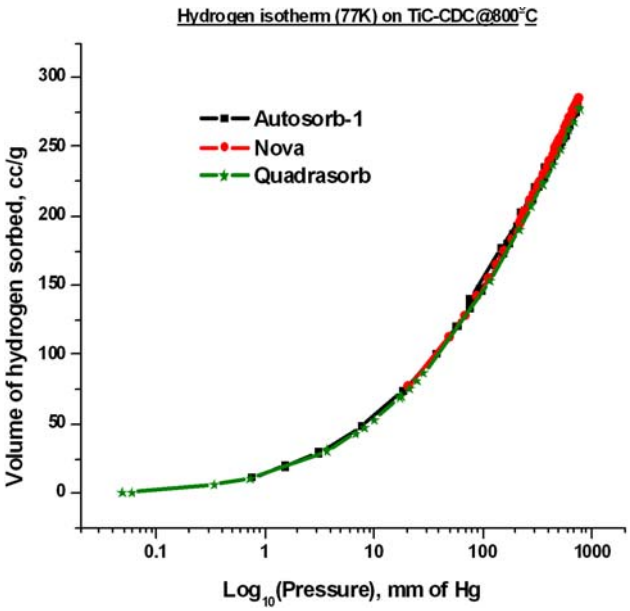


**Figure 1.** 77 K Isotherms of TiC CDC Measured by Three Different Instruments

Chemically Modified Porous Carbons

In the aforementioned CDC materials, we found that annealing in hydrogen after the chlorination treatment leads to a further 50% enhancement in hydrogen capacity, presumably by driving out the last traces of $Cl_2$ as HCl. Two other post-treatment strategies are being studied – annealing in $CO_2$ and addition of small amounts of Ti to the amorphous network. The latter approach is motivated by our theoretical study of Ti-doped SWCNT (Yildirim *et al.*, PRL **94,** 175501, 2005). Using our first-principles theoretical machinery, we demonstrated that a single Ti atom coated on a SWCNT binds up to four hydrogen molecules. The first $H_2$ adsorption is dissociative with no energy barrier, while the other three adsorptions are molecular with significantly elongated H-H bonds. At high Ti coverage we predict that Ti-modified SWCNT will strongly adsorb up to 8 wt% hydrogen. These findings will be extended to CDC carbons in parallel with new synthesis efforts.

Porous CDCs SAXS Study

We carried out a systematic SAXS study of different CDC materials, before and after activation in $CO_2$ environment. Our results demonstrate that porosity in CDC materials can be tailor-made to fit the size

of hydrogen molecule for efficient storage. Scattering techniques are non-intrusive and allow a direct analysis of pore dimensions and surface area. They are complementary to physical adsorption methods which indirectly evaluate the available pore volume through the adsorption isotherm equation. SAXS allows the determination of inhomogeneity in carbon samples over a wide size range (from few Angstroms to about hundreds of nm) and is especially required when the dimensions of the pores are the same order of magnitude as that of the probe molecules ($N_2$, $CO_2$) used in the adsorption measurements.

## Publications

1. Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium, T. Yildirim and S. Ciraci, *Physical Review Letters* 94, 175501 (2005).
2. Molecular and dissociative adsorption of multiple hydrogens on titanium-decorated $C_{60,}$ Yildirim, J. Iniguez and S. Ciraci, *Physical Review Letters* (in press).
3. Porous Carbide Derived Carbons (CDC) Optimized for Hydrogen Storage: a SAXS Study; G. Laudisio, R. K. Dash, J. P. Singer, G. Yushin, T. Yildirim, Y. Gogotsi, J.E. Fischer, accepted by the Fall MRS Symposium, Boston 11-12/2005.
4. High Hydrogen Storage in porous Carbide Derived Carbon, G. Laudisio, T. Yildirim, R. K. Dash, G. Yushin, Y. Gogotsi, J.E. Fischer, accepted by the Fall MRS Symposium, Boston 11-12/2005.
5. Nanoporous Carbide Derived Carbon with Tunable Pore Size: Synthesis and Energy-Related Applications; Gleb Yushin, John Chmiola, Ranjan K. Dash, Elisabeth Hoffman, Michel Barsoum, Yury Gogotsi,Giovanna Laudisio and John E. Fischer, invited lecture (to be presented by JEF) at the *First International Conference on Carbon for Energy Storage and Environment Protection*, Orleans France, October 2-6, 2005. Proceedings to be published in a special issue of *Carbon.*