

## IV.C.2 Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

John E. Fischer (Primary Contact),  
Yury Gogotsi, Taner Yildirim  
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

Contract Number: DE-FC36-04GO14282

Subcontractor:  
Drexel University, Philadelphia, PA

Project Start Date: October 1, 2004  
Project End Date: September 30, 2009

is working towards the former 2010 system targets including capacity targets of 6 percent hydrogen by weight and 45 grams hydrogen per liter.

### Accomplishments

- Addressed the issue of volumetric capacity of CDCs processed as powders, compacting them by rolling peels or pressing pellets; the best value to date (material only) is 29 g H<sub>2</sub>/liter.
- Also showed that chlorination of bulk ceramic monoliths preserve the excellent properties obtained from powders, along with substantial improvement in volumetric capacity.
- Found that activation of CDCs by potassium hydroxide or CO<sub>2</sub> increases the gravimetric capacity by as much as 30%, increasing the number of candidates for further optimization.
- Showed convincingly that pores <1 nm dominate the storage capacity over a range of pressures from 1 bar to 40 kbar; larger ones are less effective and mostly degrade the volumetric capacity.
- Determined that non-cubic Mo<sub>2</sub>C yields CDCs with performance rivaling those obtained with the cubic precursors TiC and SiC. This observation must be accounted for in any complete model of CDC formation.
- Showed that preceramic polymers, after pyrolysis and chlorination, yield a novel form of CDC with hierarchical porosity on several length scales, providing another synthetic path to property optimization and new applications.
- Obtained first results from neutron scattering and Hybrid Reverse Monte Carlo analysis, showing that realistic atom-scale models for CDCs can be thus obtained. An optimized 2,000-atom model for TiC-CDC chlorinated at 800°C reveals complex pore shapes which bear little resemblance to the generally-assumed slit pores based on a graphite model.
- Incremental improvements in performance metrics yield optimized materials which still fall short of the 2010 capacity goals by 15% (gravimetric) and 20% (volumetric), and only at high pressure and low temperature. Further gains will only be achieved by increasing total volume of sub-nm pores and increasing enthalpies of sorption by various doping schemes e.g. Kubas interaction. Our efforts to advance along these directions have been unsuccessful.

### 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. This project



## 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<sup>2</sup>/gram, but the enthalpy of *physisorption* is so low that reversible H<sub>2</sub> 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 H<sub>2</sub>.

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<sub>2</sub> 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.

## Approach

An excellent material family for this agenda is nanoporous 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, CDCs 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, SSA up to 2,000 m<sup>2</sup>/g, and ~80% open pore volume. 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

### Importance of Pore Size in High-pressure Hydrogen Storage by Porous Carbons

Development of high-capacity hydrogen-storage systems utilizing physisorption at high pressure and low temperature is hindered by poor understanding

of the pore size/shape requirements for achieving the maximum hydrogen uptake. Tuning the carbon structure and pore size of CDCs with high accuracy by using different starting carbides, chlorination temperatures and activation temperatures allows rational design of carbon materials with increased hydrogen-storage capacity. Systematic experimental investigation of a large number of CDCs with controlled pore size distributions and SSA shows that pores larger than 1.5 nm contribute little to hydrogen storage. It has been experimentally demonstrated that, just as at ambient pressure, pores of 0.6–0.7 nm in diameter provide the largest H<sub>2</sub> uptake per unit SSA at elevated pressures and liquid nitrogen temperatures. The effect of pore size was stronger than the effect of surface chemistry on the hydrogen uptake.

Nanoporous carbons with tunable pore size and SSA up to 3,000 m<sup>2</sup>/g available for hydrogen storage have demonstrated a gravimetric hydrogen-storage density of 4.7 wt% at elevated pressure obtained either with TiC chlorinated at 600°C activated under CO<sub>2</sub> or low temperature synthesized CDCs (400 or 500°C) activated under KOH. While small pores (1 nm or below) are efficient for hydrogen sorption and lead to an increased heat of adsorption, mesopores do not contribute much to storage of hydrogen under these conditions. Annealing of samples has shown that the pore size effect is stronger than that of functional groups on the carbon surface. A higher SSA and larger pore volume increase the hydrogen uptake for a given pore size. Our findings provide guidance for optimal design of carbon materials for high-pressure hydrogen storage at cryogenic temperatures by realizing that a large volume of small open pores with narrow size distribution is the key to high hydrogen uptake.

### CDCs with Hierarchical Porosity from a Pre ceramic Polymer

Synthesis of carbon by extraction of metals from carbides has been successfully used to produce a variety of microporous CDCs with narrow pore size distributions and tunable sorption properties. This approach is of limited use when larger mesopores are targeted, however, because the relevant synthesis conditions yield broad pore size distributions. Here we demonstrate the porosity control in the 3-10 nm range by employing pre ceramic polymer-derived silicon carbonitride (SiCN) precursors. Polymer pyrolysis in the temperature range 600 to 1,400°C prior to chlorine etching yields disordered or graphitic CDC materials with surface area in the range 800 to 2,400 m<sup>2</sup>/g. In the hierarchical pore structure formed by etching SiCN ceramics, the mesopores originate from etching silicon nitride (Si<sub>3</sub>N<sub>4</sub>) nano-sized crystals or amorphous Si-N domains, while the micropores come from silicon carbide (SiC) domains. The etching of polymer-derived ceramics allows synthesis of porous materials with a

very high specific surface area and a large volume of mesopores with well controlled size, which are suitable for applications as sorbents for proteins or large drug molecules, and supports for metal catalyst nanoparticles.

CDCs from SiCN ceramics (SiCN-CDCs) were produced by chlorination at 900°C or 1,200°C. Si and N are eliminated as SiCl<sub>4</sub> and N<sub>2</sub>, leaving behind a nanoporous network of > 98% pure carbon. Incomplete chlorination occurs at 600 and 800°C. Two types of etching reactions occur, depending on the microstructure of the SiCN ceramics, which in turn is controlled by pyrolysis temperature. At 600 to 1,200°C, pyrolysis of amorphous SiCN occurs via the decomposition reaction  $2\text{SiC}_x\text{N}_y + 4\text{Cl}_2(\text{g}) \rightarrow 2\text{SiCl}_4(\text{g}) + y\text{N}_2(\text{g}) + 2x\text{C}(\text{s})$ , while in the SiC/Si<sub>3</sub>N<sub>4</sub> nano-composite pyrolyzed at 1,400°C, these reactions occur instead:  $\text{SiC} + 2\text{Cl}_2(\text{g}) \rightarrow \text{SiCl}_4(\text{g}) + \text{C}(\text{s})$  and  $\text{Si}_3\text{N}_4 + 6\text{Cl}_2(\text{g}) \rightarrow 3\text{SiCl}_4(\text{g}) + 2\text{N}_2(\text{g})$ . In both cases Si and N are leached out, and C atoms self-organize into an amorphous or disordered, mainly sp<sup>2</sup>-bonded, structure. The characteristics of the mesoporosity can be controlled by varying the pyrolysis temperature, as this affects the microstructure of the ceramic material at the nano-scale. In the etching reaction of the nanocomposite pyrolysis products, SiC leaves behind carbon atoms, and Si<sub>3</sub>N<sub>4</sub> completely disappears, giving rise to the formation of larger pores (mesopores) and higher pore volumes.

In conclusion, chlorine etching of amorphous or crystalline polymer-derived SiCN ceramics afford CDCs possessing both micropores and mesopores with mean pore size controllable in the range 3-10 nm with Brunauer-Emmett-Teller (BET) surface area up to 2,400 m<sup>2</sup>/g. Microstructural investigations show that SiCN remains homogeneous and amorphous up to a pyrolysis temperature of 1,200°C, above which nano-crystals of Si<sub>3</sub>N<sub>4</sub>, SiC and graphite begin to form. Micropores formed by etching Si atoms from the SiC phase, while mesopores derive from the elimination of Si-N moieties. The resulting porosity (pore size, PSD, and SSA) strongly depend on pyrolysis temperature of the preceramic polymer, as well as on etching conditions. The mean pore size increases with increasing pyrolysis temperature. On the other hand, etching temperatures higher than the pyrolysis temperature do not affect the mean pore size, but leads to large BET surface area owing to the high purity. This approach can be applied to the production of porous carbon materials with very high specific surface area and large mesopore volume, potentially suitable for applications such as enterosorbents, absorption of proteins, and catalyst supports for metal particles.

### Hybrid Reverse Monte Carlo Simulations of Nanoporous Carbons

In order to develop an understanding of the link between the microstructures of microporous carbons

and their physical properties, a reconstructive reverse Monte Carlo simulation technique known as Hybrid Reverse Monte Carlo (HRMC) has been developed. It generates realistic molecular models of microporous carbon structures from experimental diffraction data. Unlike its predecessors, the HRMC method uses a many-body potential in conjunction with the reverse Monte Carlo routine to simultaneously minimize the error in fit to experimental diffraction data and the total energy of the system. This assures that resulting models capture the correct chemistry, minimizing the presence of thermodynamically unstable structures such as three and four member carbon rings.

We first applied HRMC to the well-studied TiC-CDC chlorinated at 800°C, for which a wealth of comparative data is in hand. The radial distribution function reproduced the measured neutron diffraction very accurately. In particular, unphysical high energy structures such as 3 and 4 member rings were totally absent. The pore microstructures observed in 2,000-atom models were heterogeneous, with a wide range of pore sizes with complicated pore geometries. Adsorption isotherms showed typical type I behavior expected for microporous solids.

### Conclusions

- 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.
- Bulk ceramics as well as preceramic polymers can be used as precursors for CDC synthesis, along with the more common metal carbide powders. This added flexibility provides a broader synthetic palette for optimizing CDCs with particular applications in mind.
- Spinoff startup Y-Carbon licensed to scale-up CDC manufacturing.
- Atomic-level pore structure can be found by neutron scattering and hybrid reverse Monte Carlo analysis (with Los Alamos National Laboratory and North Carolina State University).

### Special Recognitions & Awards/Patents Issued

1. The editors of Technology Review magazine named Dr. Ranjan Dash one of this year's TR35, a group of the world's top young innovators. He will be profiled in Technology Review.
2. Y-Carbon (<http://www.y-carbon.us/>) has received two SBIR Phase 1 grants from NSF and ONR, and a \$50,000 grant from Ben Franklin Technology Partners.
3. Drexel University and Y-Carbon received a 2009 R&D 100 Award for Tunable Nanoporous Carbon. The

company was founded by Trustee Chair Professor Yury Gogotsi, Dr. Gleb Yushin (currently with Georgia Tech) and Dr. Ranjan Dash to develop and commercialize nanoporous carbon processing technology.

## Publications

1. “Carbide Derived Carbon Membrane,” E.N. Hoffman, G. Yushin, B.G. Wendler, M.W. Barsoum, Y. Gogotsi, *Materials Chemistry and Physics*, **112**, 587-591 (2008).
2. “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* **116**, 469–472 (2008).
3. “Carbide Derived Carbon and Templated Carbons,” T. Kyotani, J. Chmiola, Y. Gogotsi, Chapter 3 in *Carbons and Composites for Electrochemical Energy Storage Systems*, edited by F. Beguin and E. Frackowiak, CRC Press/Taylor and Francis, pp. 77-113 (2009).
4. “Porosity control in nanoporous carbide-derived carbon by oxidation in air and carbon dioxide”, S. Osswald, C. Portet, Y. Gogotsi, G. Laudisio, J.P. Singer, J.E. Fischer, V.V. Sokolov, J.A. Kukushkina, A.E. Kravchik, *Journal of Solid State Chemistry* (2009), doi:10.1016/j.jssc.2009.04.017.
5. “Hybrid Reverse Monte Carlo Simulations of Nanoporous Carbons”, J.C. Palmer, S.K. Jain, K.E. Gubbins, N. Cohaut, J.E. Fischer, R.K. Dash and Y. Gogotsi, in *Characterization of Porous Solids VIII, Proceedings of the 8<sup>th</sup> International Conference on Characterization of Porous Solids*, Eds. S. Kaskel, P. Llewellyn, F. Rodriguez-Reinos and N.A. Seaton, pp. 56-63, Royal Society of Chemistry, Cambridge, Special Publication No. 318 (2009).
6. “Molybdenum carbide-derived carbon for hydrogen storage”, H.S. Kim, J.P. Singer, Y. Gogotsi and J.E. Fischer, *Mesoporous and Microporous Materials* **120**, 267-271 (2009).
7. “Enhanced methane storage of chemically and physically activated carbide-derived carbons”, S. Yeon, S. Osswald, Y. Gogotsi, J.P. Singer, J.M. Simmons, J.E. Fischer, M.A. Lillo-Rodenas, A. Linares-Solano, *J. Power Sources* **191**, 560 (2009).
8. “Capacitance of KOH Activated Carbide-Derived Carbons”, C. Portet, M.A. Lillo-Rodenas, A. Linares-Solano, Y. Gogotsi, *Physical Chemistry Chemical Physics* **11**, 4943-4945 (2009).
9. “Importance of Pore Size in High Pressure Hydrogen Storage by Porous Carbons”, Y. Gogotsi, C. Portet, S. Osswald, J. Simmons, T. Yildirim, G. Laudisio, J.E. Fischer, *International Journal of Hydrogen Energy* (2009), doi:10.1016/j.ijhydene.2009.05.073.
10. “Carbide-Derived-Carbons with Hierarchical Porosity from a Pre-ceramic Polymer”, S.-H. Yeon, P. Reddington, Y. Gogotsi, J.E. Fischer, C. Vakifahmetoglu, and P. Colombo, *Carbon* (under review).

## Presentations

1. J.E. Fischer, *Porous Carbons for Hydrogen Storage: Physics, Chemistry and Prospects*, Georgetown University, Oct. 9, 2008.
2. J. Chmiola, Y. Gogotsi, C. Largeot and P. Simon, *Monolithic Carbide-derived Carbon Films with Superior Volumetric Capacitance*, 214<sup>th</sup> Electrochemical Society Meeting, October 12–16, 2008, Honolulu, HI
3. Y. Gogotsi, *Nanostructured Carbons for Energy-Related Applications*, EPRI Workshop Materials for Next Generation Energy Storage, October 20–21, 2008, Cleveland, OH.
4. Y. Gogotsi, *Nanostructured Carbide-Derived Carbons for Energy-Related and Biomedical Applications*, RUSNANOTECH, Moscow, Dec. 2-6, 2008.
5. S.-H. Yeon, P.Reddington, P. Colombo, J. E. Fischer, Y.Gogotsi, *High Specific Surface Area Carbon from Etching of SiCN Ceramics*, 33<sup>rd</sup> International Cocoa Beach Conference on Advanced Ceramics and Composites, Daytona Beach, FL, January 2009.
6. Y. Gogotsi, *Carbide-Derived Carbons: From Nanotubes to Porous Networks* Clemson University, SC, March 6, 2009. Y. Gogotsi, *Carbide-Derived Carbons for Energy Related Applications*, Imperial College, London, March 9, 2009.
7. Y. Gogotsi, *Carbide Derived Carbon as Biological Enterosorbent and Adsorbent for Hemoperfusion*, University of Brighton, Brighton, UK, March 11, 2009.
8. Y. Gogotsi, *Carbide-Derived Carbons for Supercapacitors and other Energy Related Applications*, University of Albany, SUNY, March 13, 2009.
9. S. Osswald, Y. Gogotsi, *Thermal Analysis of Oxidation of Carbon Nanomaterials*, Thermal Science from the Micro- to Nanoscale, Philadelphia, March 27, 2009.
10. Y. Gogotsi, *Carbide-Derived Carbons for Energy Related Applications*, Texas A&M, College Station, TX, April 3, 2009.
11. Y. Gogotsi, *Design of Nanostructured Carbons for Energy Storage*, Oak Ridge National Laboratory, Oak Ridge, TN, May 7, 2009.
12. Y. Gogotsi, *Carbide-Derived Carbons for Energy Related Applications*, University of Tennessee, Knoxville, May 8, 2009.
13. J. Palmer, S.-H. Yeon, A. Llobet, K.R. Gubbins, J.E. Fischer and Y. Gogotsi, *Molecular Modeling and Simulation of Titanium Carbide Derived Carbons*, Pacific Basin Conference on Adsorption Science and Technology, Singapore, May 2009.
14. A. Llobet, J.C. Palmer, S-H. Yeon, J.E. Fischer, Y. Gogotsi, K.E. Gubbins, *Local Structure of Microporous Carbide-Derived Carbons from Scattering Experiments and Modeling*, CARBON'09, The Annual WORLD CONFERENCE on CARBON, Biarritz, France, June 14–19, 2009.

**15.** C. Portet, M.A. Lillo-Rodenas, A. Linares-Solano, Y. Gogotsi, *KOH Activated Carbide-Derived Carbons as Electrodes for Electrochemical Capacitors*, CARBON'09, The Annual WORLD CONFERENCE on CARBON, Biarritz, France, June 14–19, 2009.

**16.** S.-H. Yeon, S.Osswald, Y. Gogotsi, J. P. Singer, J.M. Simmons, J.E. Fischer, M.A. Lillo-Ródenas, A. Linares-Solano, *Enhanced Methane Storage of Chemically and Physically Activated Carbide-Derived Carbon*, 5th Workshop on Porous Materials, New Brunswick, NJ, July 2009.