



2006 DOE Hydrogen Program

Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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Project ID #
ST21

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Overview

Timeline

- Project start: Oct 2004
- Project end: Sept 2008
- 40% Complete

Budget

- Total project funding (expected)
 - DOE - \$ 1,440 K
 - Contractor - \$ 370 K
- Funding received in FY05
 - \$ 300 K
- Funding for FY06 (to date)
 - \$ 225 K

Barriers & Targets

- Barriers we are addressing:
 - A. System Weight and Volume
 - F. Lack of Understanding of Hydrogen Physisorption and Chemisorption
 - Q. Reproducibility of Performance.
- Targets: gravimetric and volumetric capacity, operability and cost.

Interactions/ collaborations:

Quantachrome, IPNS (Argonne), NIST



Objectives

- Develop and demonstrate efficient, durable and reversible hydrogen storage in carbide-derived carbons (CDC) with tunable nanoporosity (2004-2005).
- Determine the optimum pore size for hydrogen storage using experiment and theory (2005-2006).
- Identify post-processing strategies and catalytic additives which maximize the performance of CDC-based hydrogen storage materials, using experiment and theory (2006-2007).
- Finalize the design of a CDC-based H₂ storage material that meets 2010 DOE performance targets and commercialize it (2007-2008).

Approach

Determine which parameters are important for H₂ adsorption



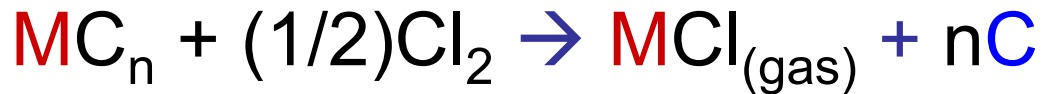
Synthesize CDC with pore size optimized for high H₂ adsorption



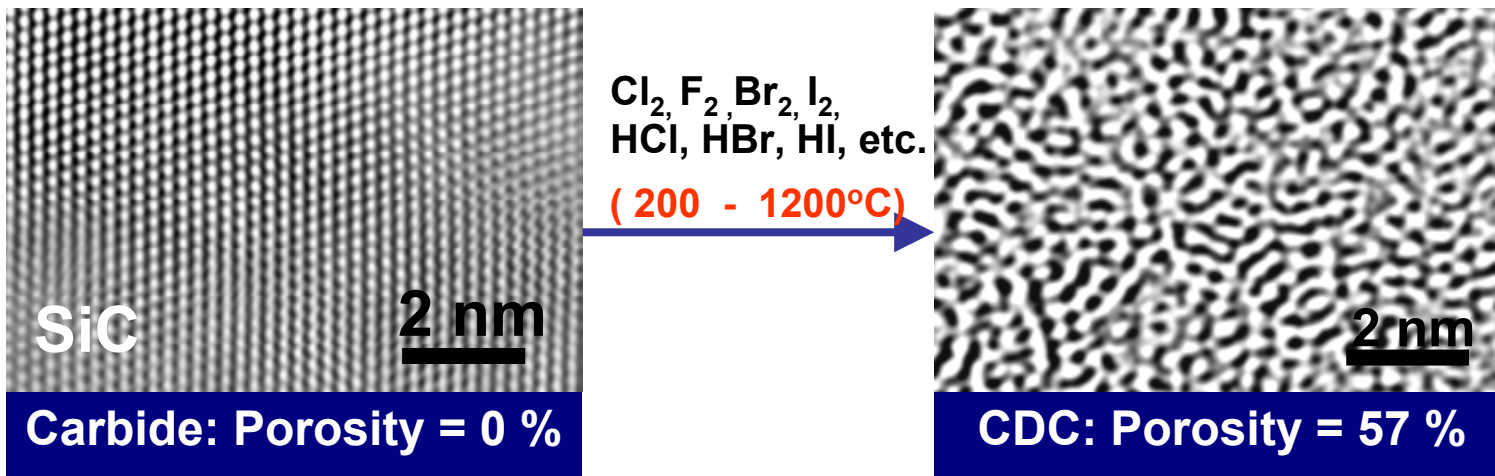
Increase the volume of optimally sized pores



Increase heat of adsorption for storage at or near 300K

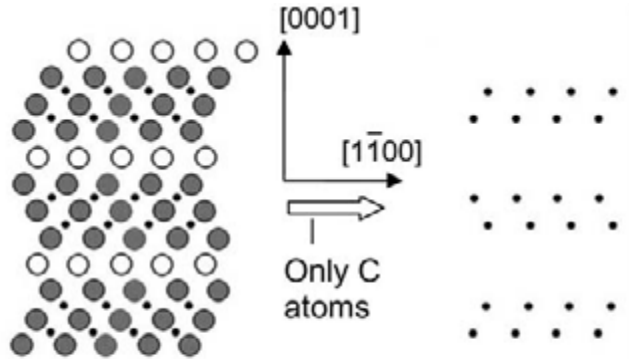


M = metal or metalloid, C = carbide-derived carbon



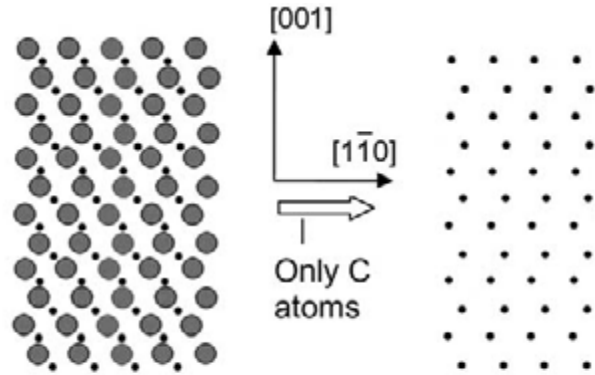
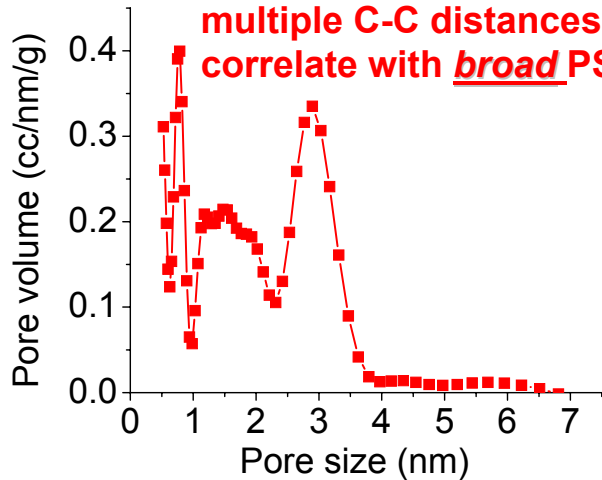
- Over 30 different CDC materials synthesized and evaluated

Unique features of CDC



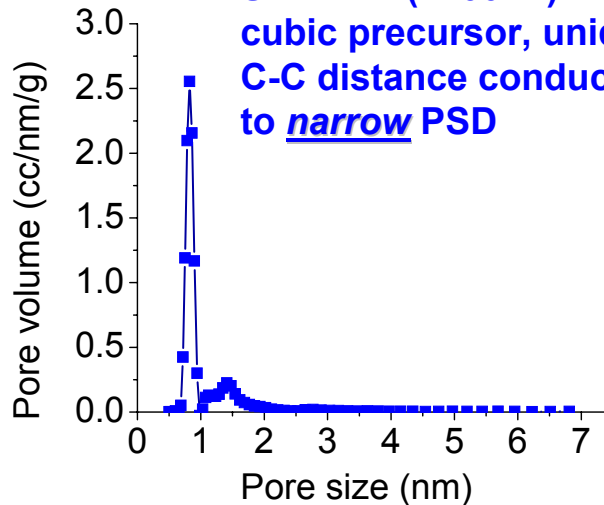
[11 $\bar{2}$ 0] projection of Ti_3SiC_2
 ● Ti ○ Si • C

Ti_3SiC_2 -CDC (1200°C):
 orthorhombic precursor,
 multiple C-C distances
 correlate with broad PSD



[110] projection of 3C-SiC
 ● Si • C

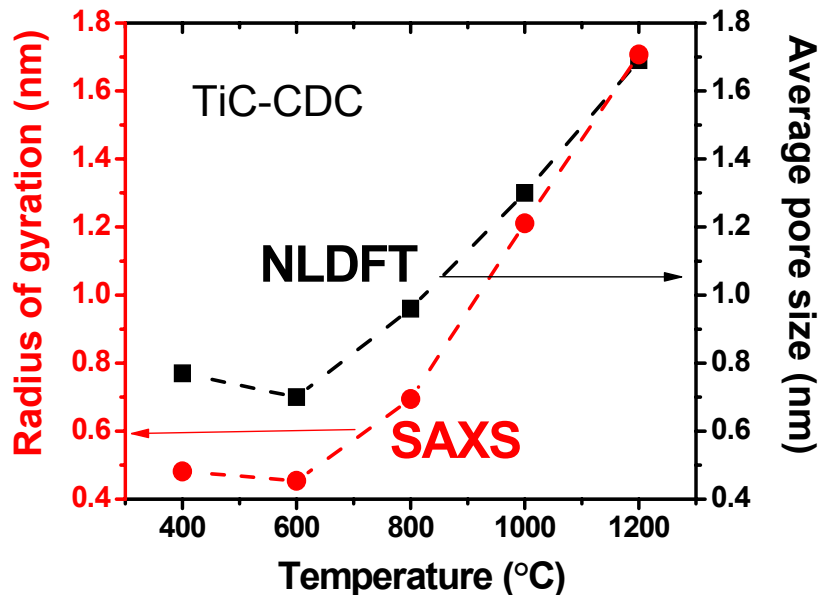
SiC-CDC (1200°C):
 cubic precursor, unique
 C-C distance conduces
 to narrow PSD



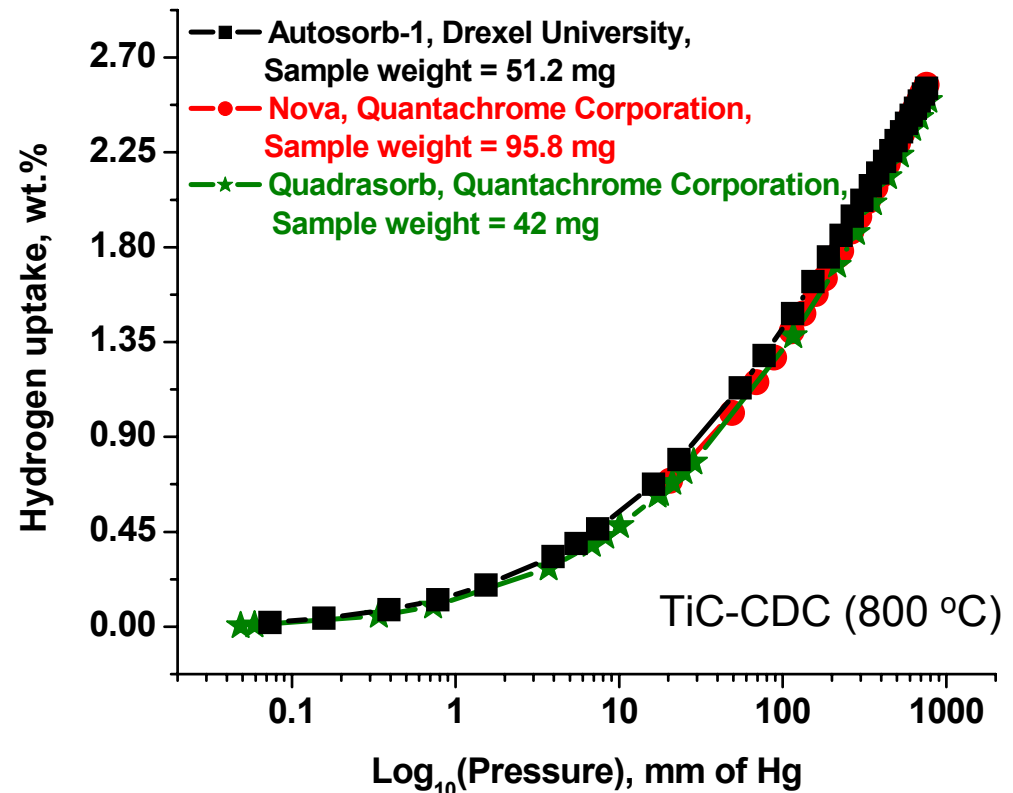
- Precise control over structure and pore size distribution by varying:
 - rxn temperature
 - precursor carbide
 - synthesis environment
 - post-treatments
- Uniform pore size can be achieved, an important requirement for studying sorption fundamentals systematically.
- Free- standing monoliths can be processed for **high volumetric capacity**.
- Economical: many precursors are cheap; simultaneous production of metal chlorides.

Methods and Reproducibility

- gas adsorption (Ar/CO₂/N₂/H₂):
- specific surface area (SSA) & pore size
- small angle x-ray scattering (SAXS):
- pore size and total pore volume
- local atomic structure from neutron pdf
- prompt-gamma activation analysis (PGAA): impurities, doping concentrations
- modeling



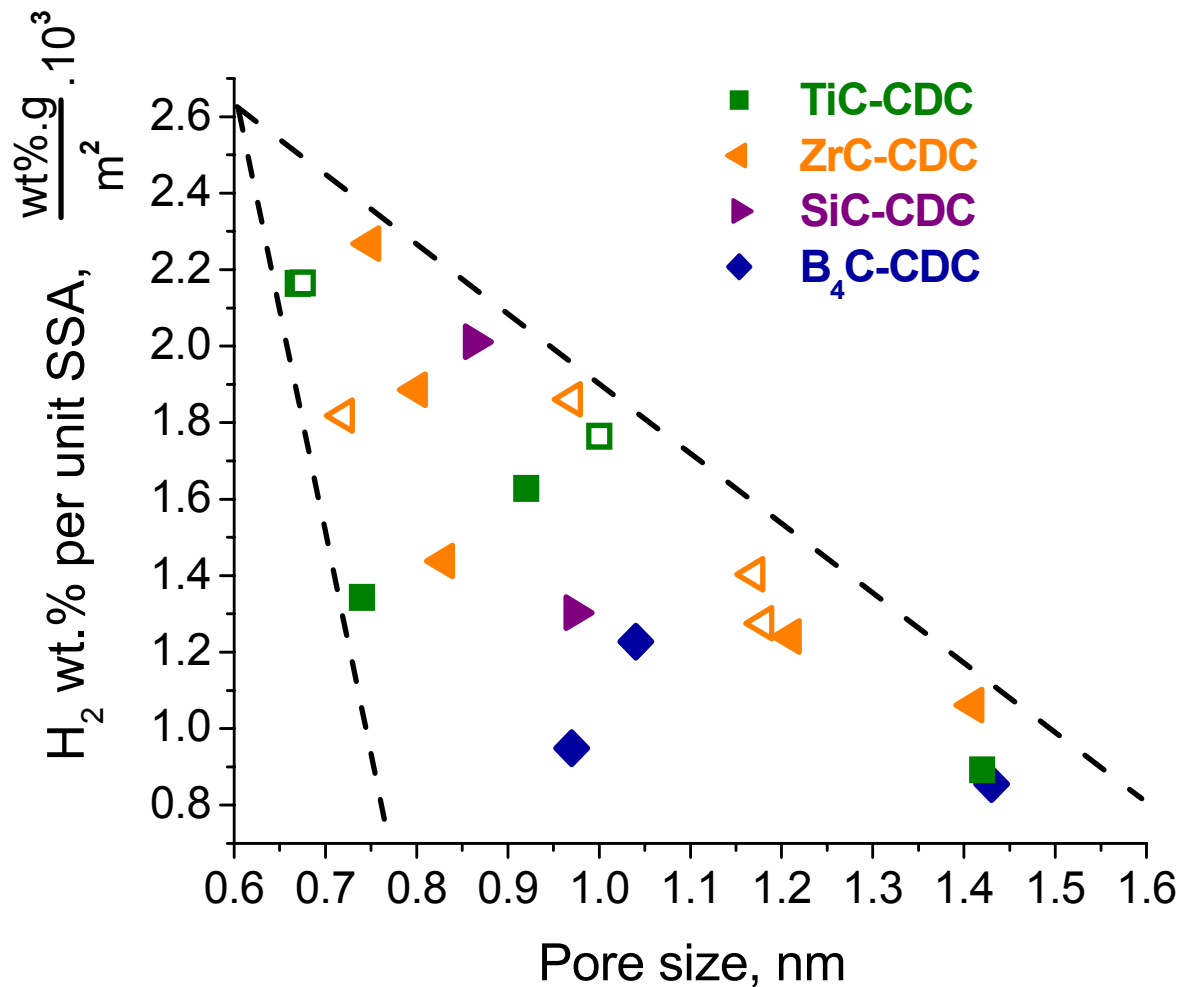
- H₂ storage results reproduced using different instruments at Drexel, NIST, and Quantachrome, Inc.
- Repeat identical syntheses give $\pm 5\%$ variations in H₂ capacity.



Lacking **direct** probes of micropores, the agreement between two indirect methods gives added confidence in the results

Progress / Results

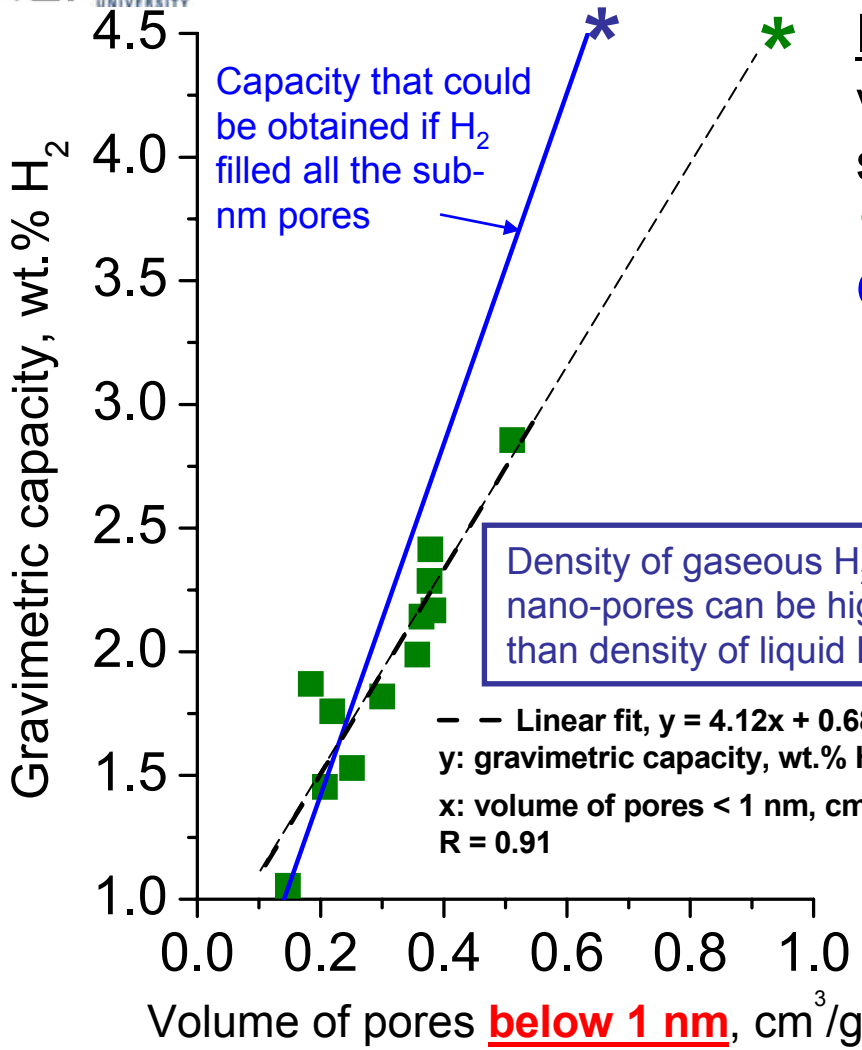
H₂ uptake at 1 atm, 77K



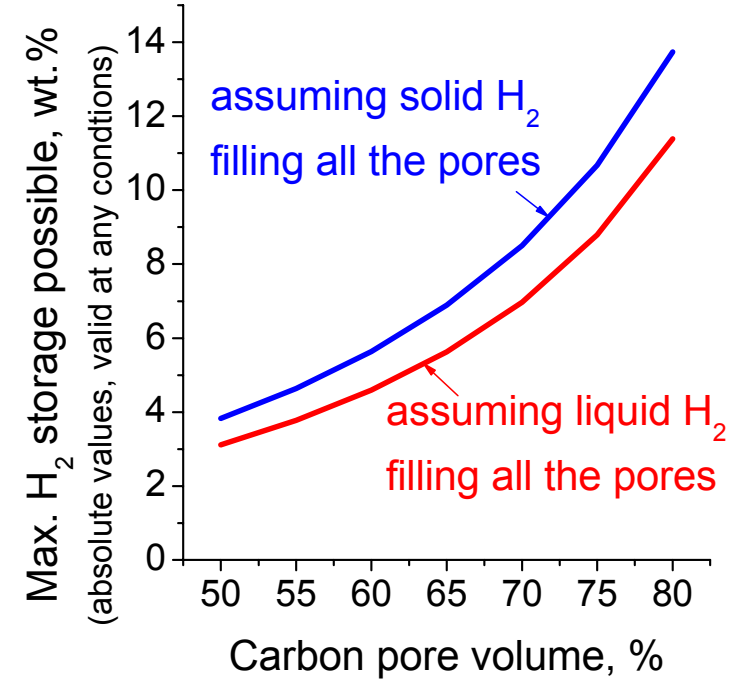
- Subnanometer pores are more efficient than large ones for H₂ adsorption on carbon surfaces
- Subnanometer pores are obtained from fcc TiC, ZrC.
- SSA of ~2600 m²/g required for 6 wt% at 1 atm. and 77K.
- Large pores decrease the volumetric capacity.
- Annealing in hydrogen (open symbols) removes residual Cl₂, increasing the pore volume available for storage.



Progress / Results



Extrapolation: CDC with 0.92 cm³/g pore volume (67% porosity) gives 4.5 wt.% H₂ storage if all pores are < 1 nm, **even at 1 atm, where all the pores are not filled.** Only ~0.6 cm³/g needed if **all** pores filled.

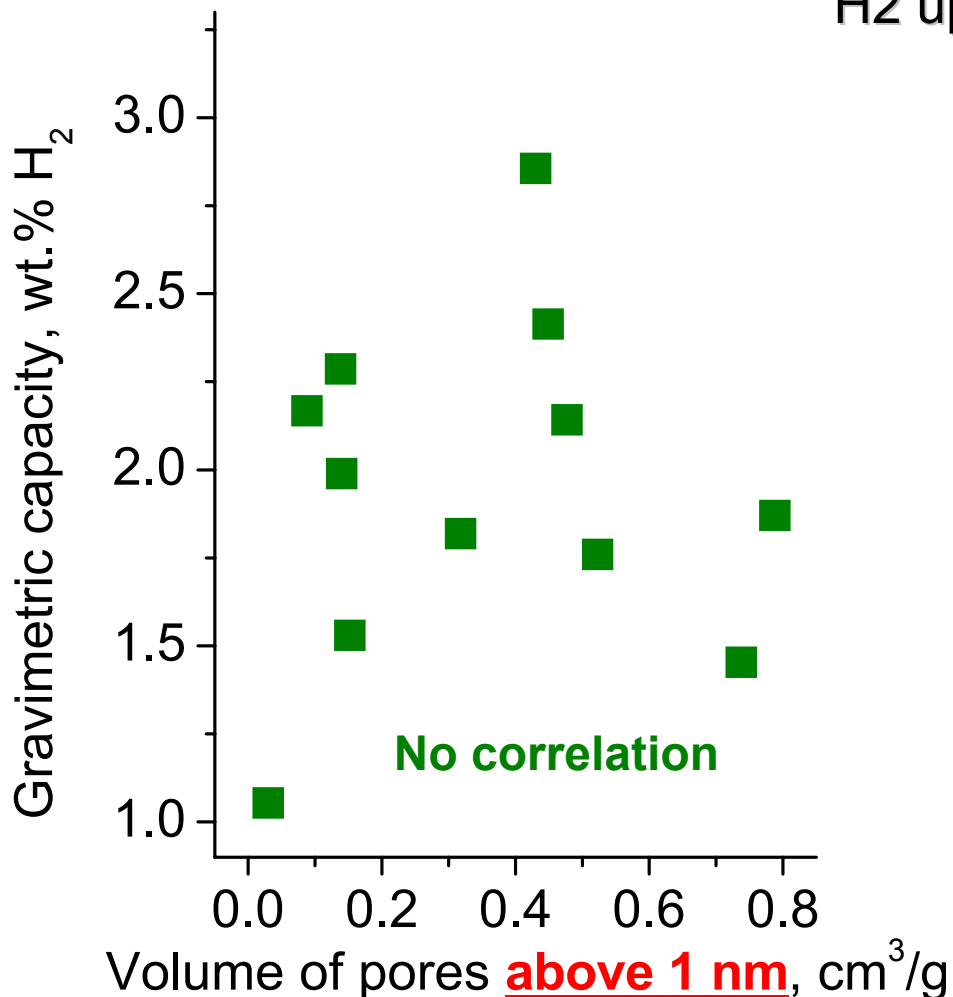


STRONG CORRELATION BETWEEN CAPACITY AND VOLUME OF SMALL PORES

[1] J. Jagiello et al., *J. Phy. Chem. B*, in press (2006)
[2] Q. Wang et al., *J. Chem. Phys.* 110, 577-586 (1999)

Progress / Results

H₂ uptake at 77K, 1 atm

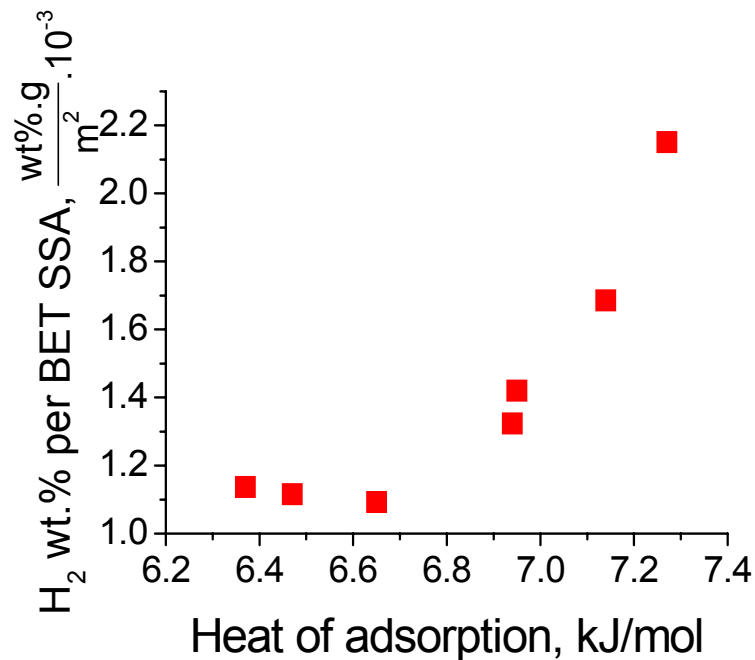
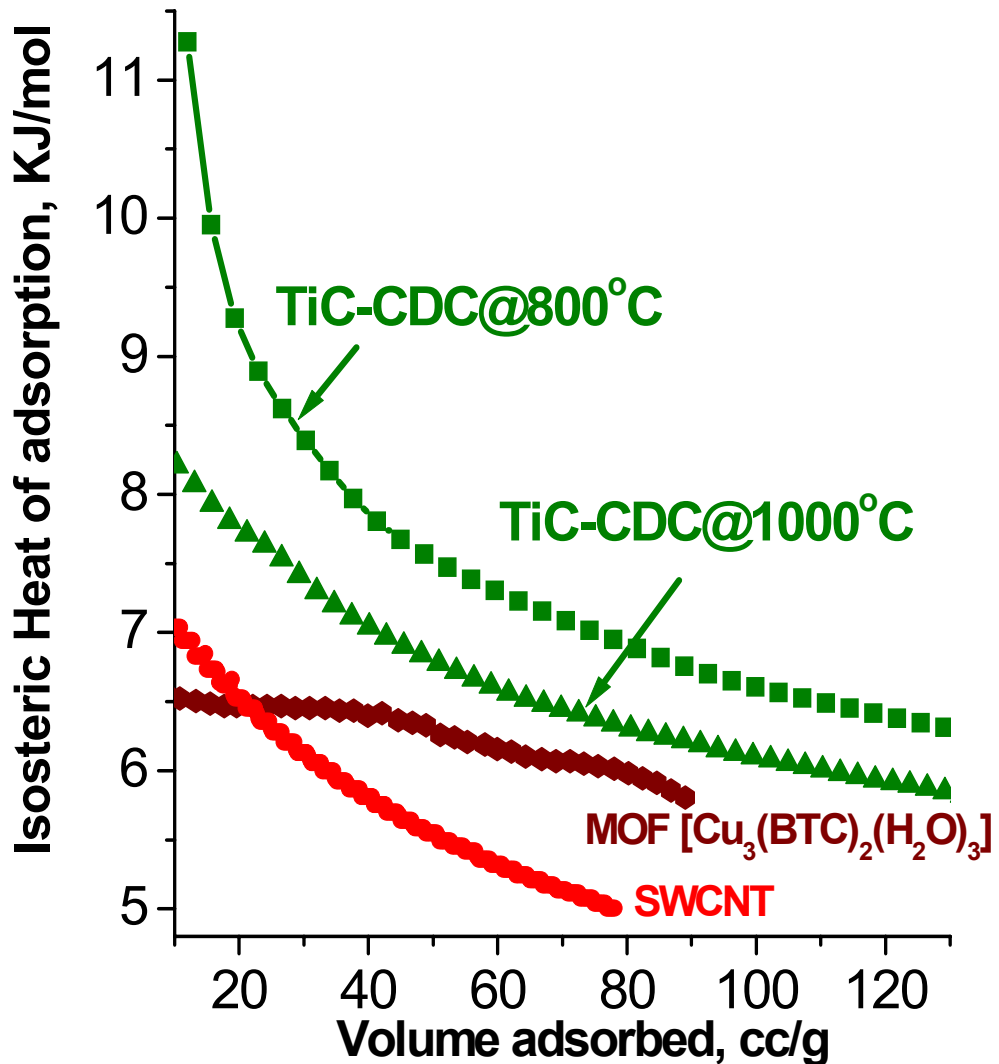


➤ Large pores are much less useful for H₂ storage (they are not efficient in terms of surface coverage by H₂ atoms; they also degrade volumetric capacity since adsorption is generally limited to a surface monolayer)

➤ CDC with only modest SSA (< 1300 m²/g) but with small pores substantially outperformed others with SSA > 2300 m²/g but having wider pore size distribution (PSD).

Progress / Results

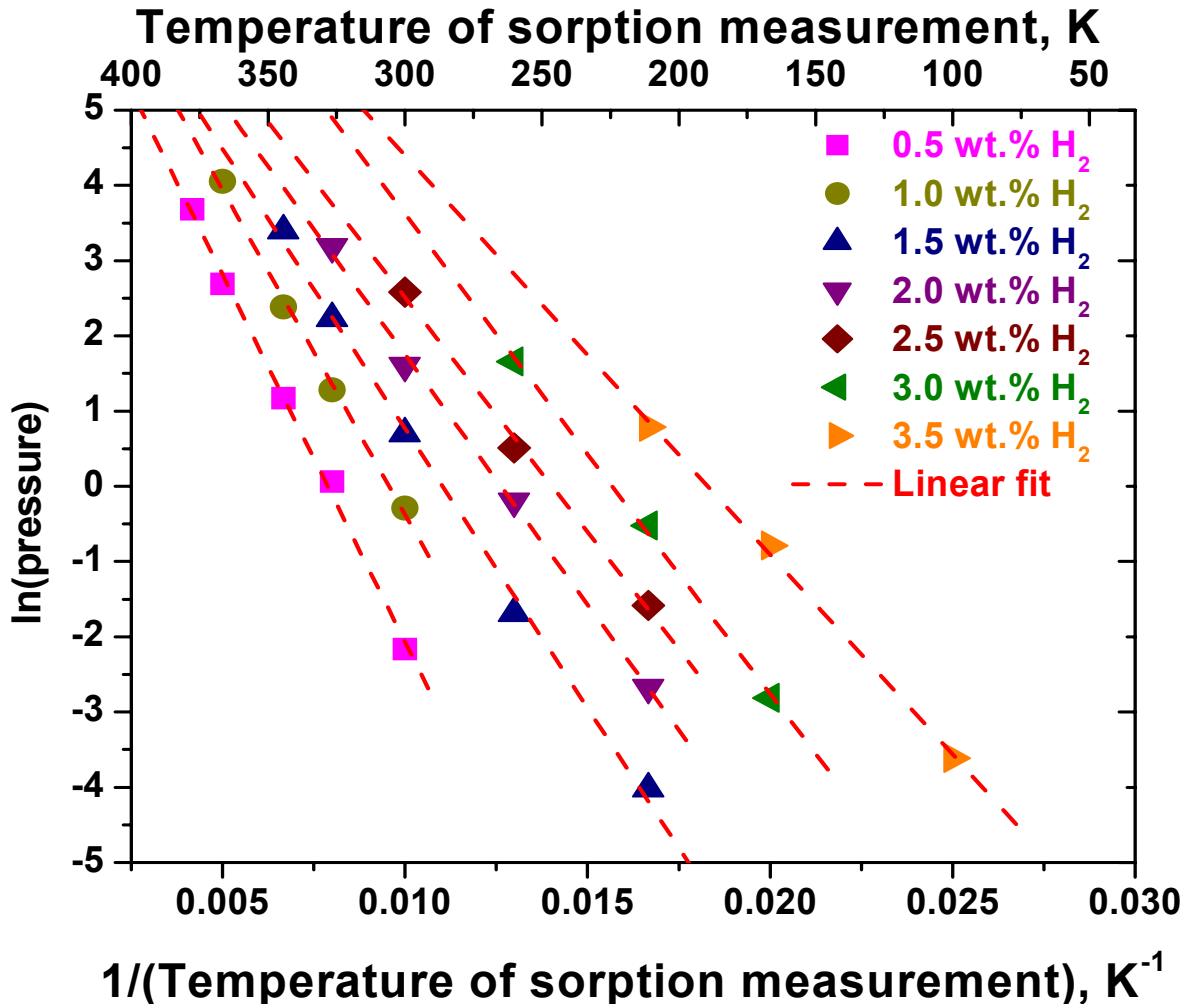
H₂ uptake at 1 atm



- Small pores increase the interaction with H₂ (higher heat of adsorption) and thus result in higher H₂ coverage of the sorbent surface
- CDC demonstrates a stronger interaction with H₂ than CNT or MOF

Progress / Results

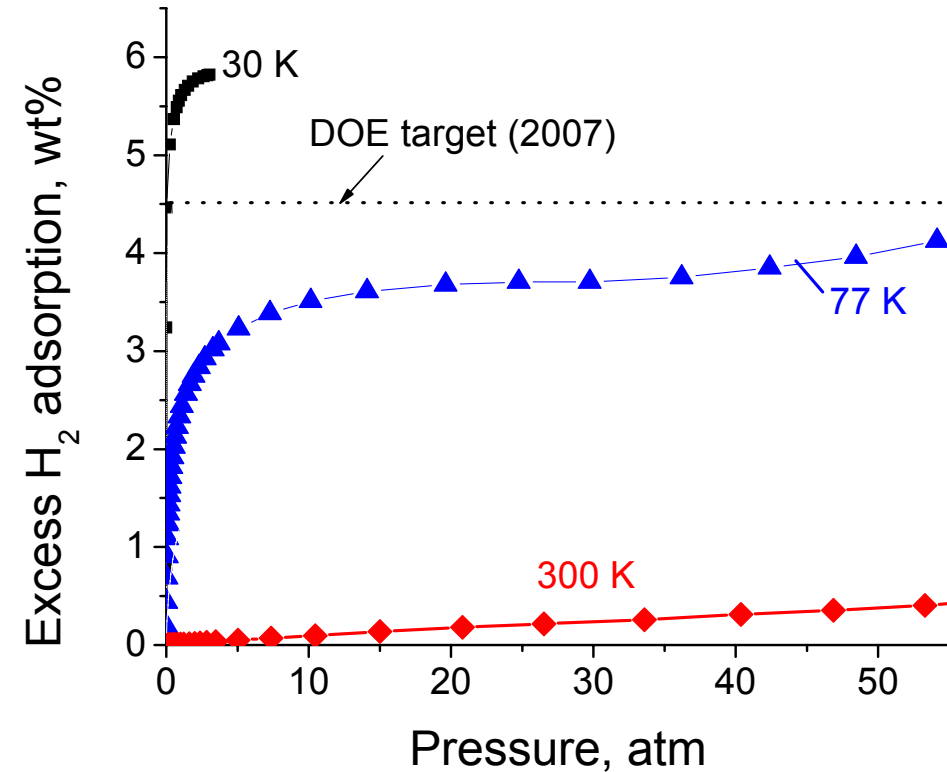
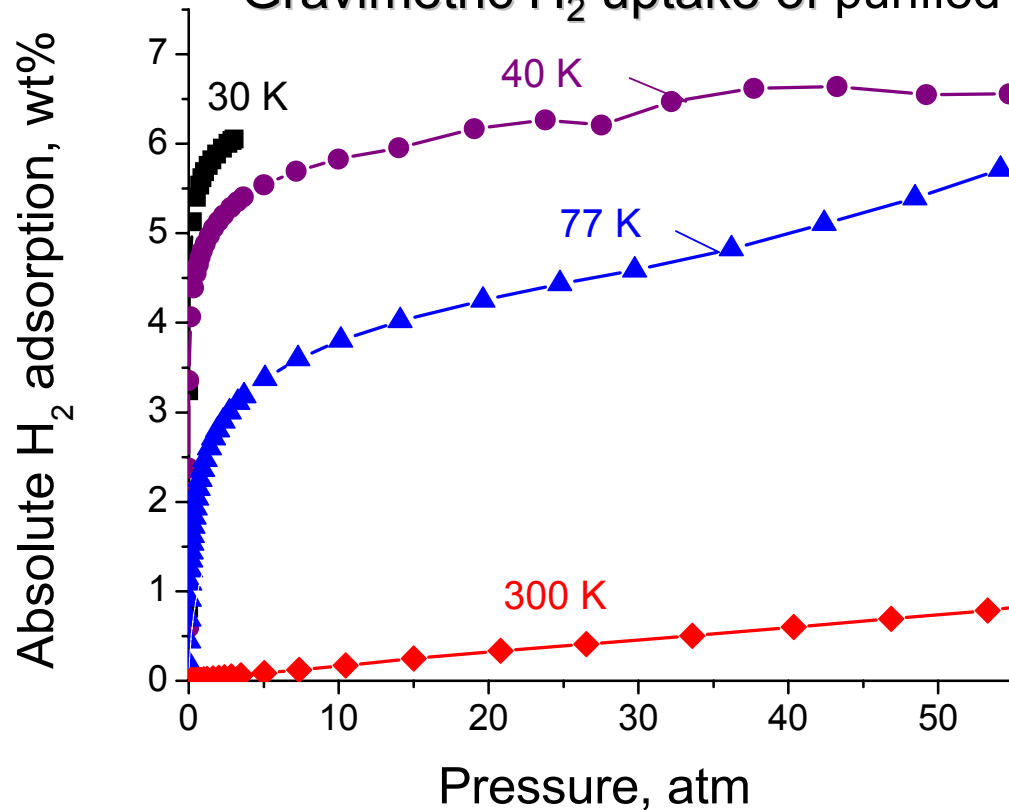
Heat of adsorption is independent of temperature



Since the heat of adsorption does not depend on temperature, values obtained from measurements at 77-87K and low pressure are valid at room temperature and elevated pressures.

Progress / Results

Gravimetric H₂ uptake of purified TiC CDC at high pressures



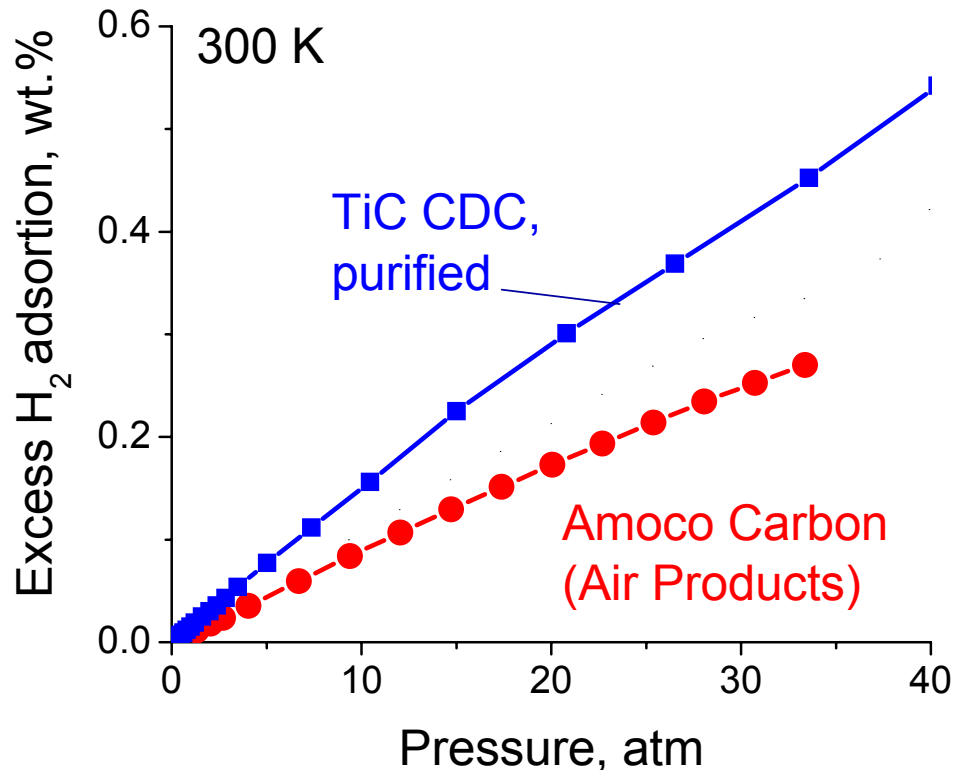
➤ Small pores allow CDCs to achieve high uptake at moderate pressures

➤ CDC approach 2007 DOE target*
 ➤ Increased pore volume and smaller pore size needed to boost excess H₂ capacity.

* Data assume material only

Progress / Results

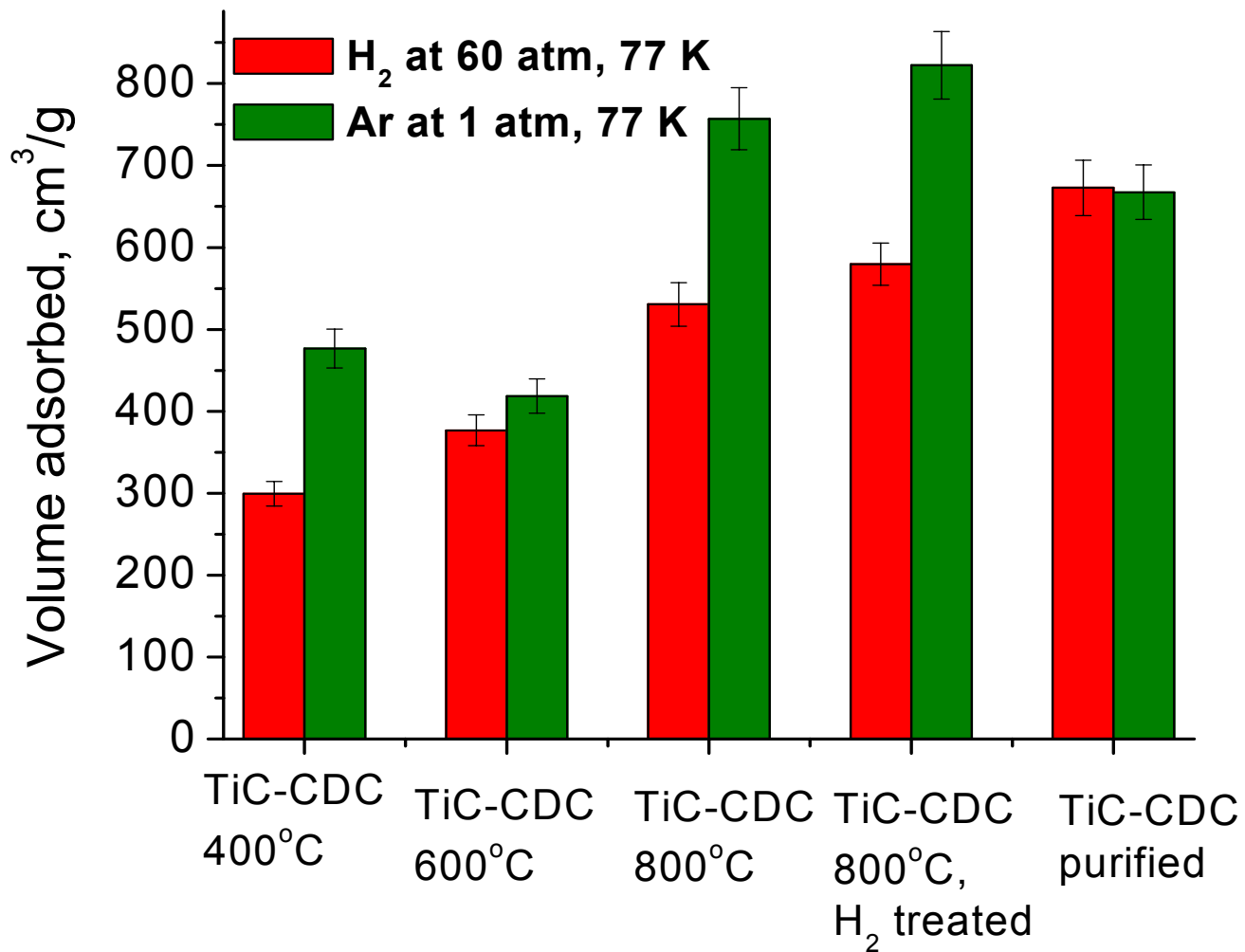
Comparison with advanced activated carbons



➤ At room temperature CDC demonstrates performance superior to that of activated carbons

High pressure measurements of Amoco Activated Carbon were done by VTI, Inc. 7650 West 26th Ave., Hialeah, FL 33016

Progress / Results

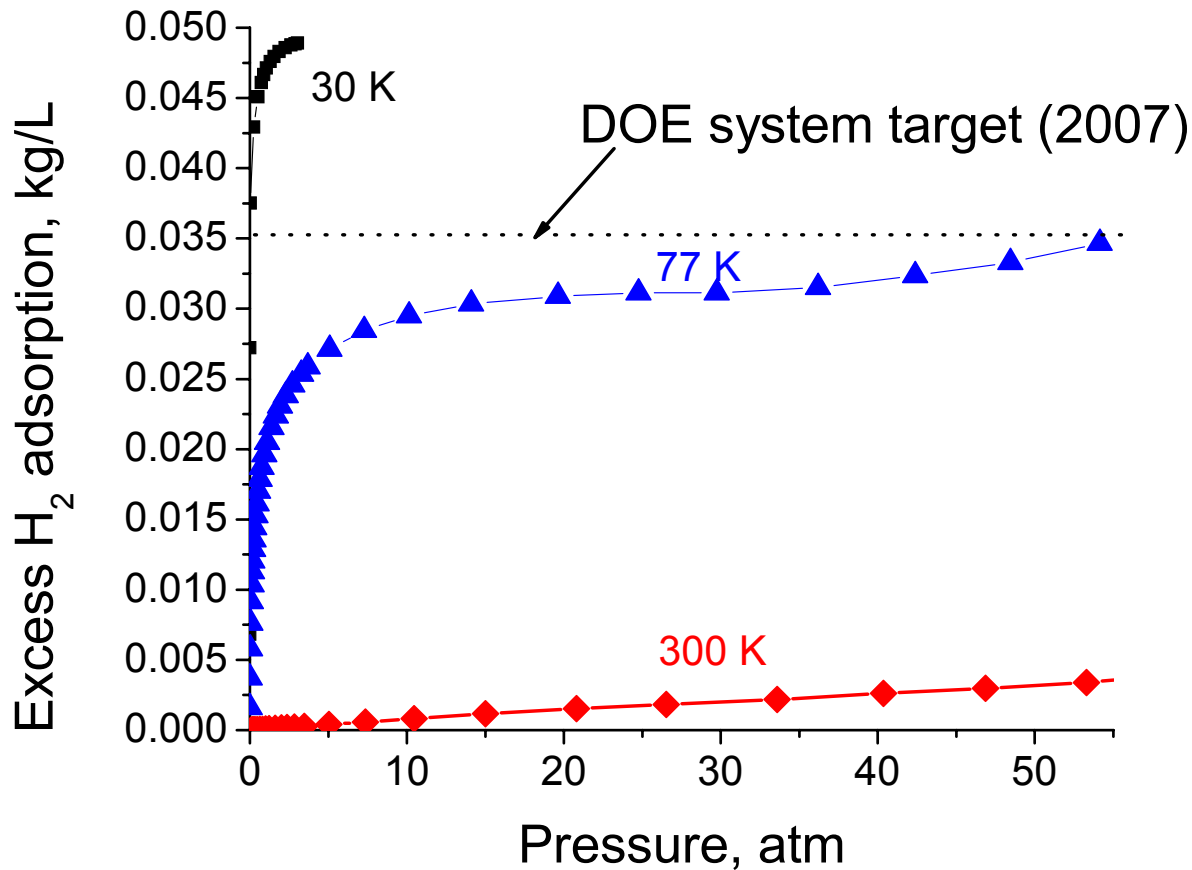


➤ Filling all the pores with densely packed H₂ is possible at high pressure (60 atm, 77K)

➤ Larger pore volume is required to increase gravimetric uptake.

Progress / Results

Volumetric H₂ uptake of CDC at high pressure



➤ Ideal volumetric capacity of CDC approaches 2007 DOE target.

➤ Possibility to produce CDC in monoliths with very small fraction of macropores gives it an advantage over other high SSA H₂ storage media in terms of volumetric performance

Volumetric calculations assume a CDC density of 0.84 kg/L, corresponding to the carbon skeleton of cubic TiC with no macroscopic collapse (conformal reaction). Intergranular voids in powdered materials are neglected.



Future Work

- Increase volume of subnanometer pores to $0.9 \text{ cm}^3/\text{g}$ to achieve $> 6 \text{ wt.}\%$ at 77 K and 40 atm or less, using conventional and novel activation techniques (12/2006).
- Increase average heat of adsorption to improve H_2 storage at temperatures above 77 K, and eventually RT.
- Set up theoretical models to predict doping candidates (60% done).
- Synthesize doped CDC and CDC containing catalyst particles for further improved H_2 uptake (03/2007).
- Synthesize gram quantities of selected CDCs for round-robin testing and evaluation (09/2006) - fluidized bed reactor (2-20 g/run) designed and under test.
- Understand in detail, from theory and experiment, the hydrogen-carbon interaction (09/2007).
- First-principles molecular dynamics simulations to guide improved storage dynamics (09/2007).
- Achieve commercialization and scale-up; seek commercial partner (09/2008).



Near term

- Push towards 300K operation by **increasing the heat of adsorption**. We will exploit unique metal-hydrogen interactions in a structurally-optimized system. So far, theory and modeling of **Ti dopants** on nanotube and C_{60} surfaces (Yildirim) show that these structures are too open to avoid metal segregation. On the other hand, CDC with the right pore volume and PSD should be perfect for doping with light transition metals; pores in CDC are zero-D, so Ti can't migrate from pore to pore.
- Develop post-processing strategies to **improve utilization of total pore volume** for hydrogen storage. First success – annealing in H_2 to clean out residual Cl_2 . Develop new approaches to remove amorphous carbon blocking pores and create additional small pores.
- **Direct measurements of gravimetric capacity** on pelletized CDC powders. Find critical density at which we start losing capacity due to pore collapse, impeded diffusion and/or prohibitively slow sorption/desorption kinetics.
- New theoretical approaches to treat noncrystalline systems – **direct visualization of carbon collapse inside “vacated” carbide** to create pore structure; correlation of pore size/shape with precursor crystal symmetry.
- Reverse Monte Carlo analysis of neutron scattering, to **help identify pore size and shape**.



Summary

Relevance: Adsorption of H₂ in porous carbon was evaluated. Parameters governing adsorption investigated.

Approach: A family of novel carbon materials with controllable porosity and microstructure (CDC) synthesized.

Technical Accomplishments and Progress: Excess H₂ adsorption over 4.3 wt.% and 0.034 kg (H₂)/L was demonstrated in CDC @ (77K, 55 atm). Max heat of H₂ adsorption up to 11 kJ/mol (with average values ~ 8 kJ/mol) demonstrated.

Proposed Future Research: Further modification of CDC porosity, microstructure and chemistry for improved H₂ uptake.

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Publications and Presentations

PAPERS:

1. Tailoring of Nanoscale Porosity in Carbide-Derived Carbons for Hydrogen Storage , Y. Gogotsi , 2. R.K. Dash, G. Yushin, T. Yildirim, G. Laudisio, J.E. Fischer, *J. Am. Chem. Soc.* **127**, 16006-16007 (2005).
2. Molecular and Dissociative Adsorption of Multiple Hydrogens on Titanium-decorated C₆₀, T. Yildirim, J. Iniguez and S. Ciraci, *Phy. Rev Letters* (in press).
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.* (submitted).
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* (submitted).

PRESENTATIONS:

1. 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, invited talk at Fall MRS Symposium, Boston 11-12/2005.
2. High Hydrogen Storage in porous Carbide Derived Carbon, G. Laudisio, T. Yildirim, R. K. Dash, G. Yushin, Y. Gogotsi, J.E. Fischer, Fall MRS Symposium, Boston 11-12/2005
3. 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 at the First International Conference on Carbon for Energy Storage and Environmental Protection, Orleans France, October 2-6, 2005.
4. Carbide-derived Carbons with Tailored Porosity Optimized for Hydrogen Storage , Y. Gogotsi, R.K. Dash, G. Yushin, T. Yildirim, G. Laudisio and J.E. Fischer, invited speaker, Hydrogen Storage with Novel Materials, Bad Honnef, Germany, Oct 23-27, 2005.
5. 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 4/2006.
6. Tailored nanoscale porosity in carbide-derived carbons: optimization for high capacity hydrogen storage, invited talk at *MH2006* (Metal-Hydrogen interactions), Maui (October 1-4, 2006).



Distribution of effort

University of Pennsylvania

Small angle X-ray scattering (SAXS)

Transmission electron microscopy (TEM)

Pore volume / pore size design

Post-synthesis activation, doping

Drexel University

Material synthesis

Structural characterization (Raman spectroscopy, X-ray diffraction)

Porosity analysis using gas sorption technique

Low pressure (1 atm) hydrogen storage measurements

NIST

High pressure hydrogen storage measurements

Neutron scattering studies

Simulations using density functional tight binding (DFTB) method

Critical Assumptions and Issues

- Achieve gravimetric capacity requirements. We assume this can be done by enhancements in pore volume. Same applies to MOFs and other cryosorbers. Other solutions outside the scope of our project are to use chemical storage methods, e.g. alanates.
- Achieve volumetric requirements. We assume this can be done by optimizing PSD. MOFs suffer more from this issue than do the various carbons. Chemical storage materials will have no problem meeting volumetric requirements.
- Achieve storage at modest temperatures and pressures, with no significant thermal load on the system. We assume we can accomplish this by enhancing the heat of adsorption and optimizing PSD. MOF's with bigger pores will always require high pressures. Chemical storage methods all require cooling to dissipate heats of decomposition when the hydrogen is released.