



Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

John E. Fischer^{1,3}, Yury Gogotsi², and Taner Yildirim^{3,1}

¹*Department of Materials Science and Engineering
University of Pennsylvania,
Philadelphia, PA 19104*

²*Department of Materials Science and Engineering
Drexel University
Philadelphia, PA 19104*

³*National Institute of Standards and Technology
Gaithersburg, MD 20899*

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Project ID:
ST-09



Overview

Timeline

- Project start: Oct 2004
- Project end: Sept 2008
- 75% complete

Budget

- Total project funding (expected)
 - DOE - \$ 1,440 K
 - Contractor - \$ 370 K
- Funding received in FY06
 - \$ 275 K
- Funding for FY07 (to date)
 - \$ 175 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.

Collaborations

IPNS, U. North Carolina – local structure
NIST – neutron scattering
Quantachrome, Arkema, R. Chahine – validation of sorption results



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).

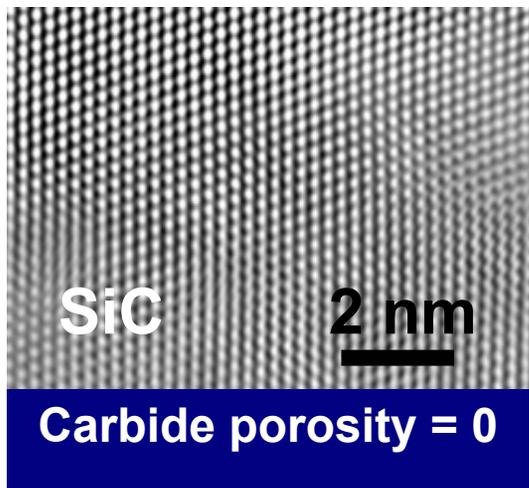
Approach

- Create “designer” pore structures in amorphous carbon by etching metals out of crystalline metal carbide precursors (binary, ternary, alloys, powders, monoliths...) using chlorine at ~ 1 atm., 300-1200C.
- Optimize pore size and shape, size distribution, total volume and specific surface area by choice of precursor (crystal symmetry plays a role), and synthesis conditions (temperature, time, flow rate).
- Develop post-chlorination treatments to further enhance pore volume and surface area, and to optimize binding and release energetics for cycling at reasonable T and P.

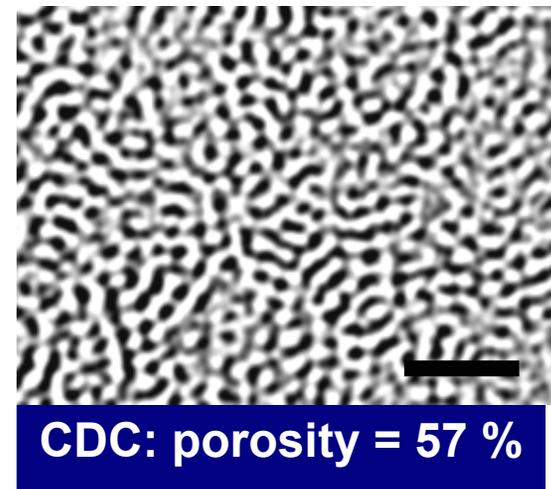
Example: $MC + (1/2)Cl_2 \rightarrow MCl(\text{gas}) + C$,

M = metal or metalloid

C = carbide-derived carbon



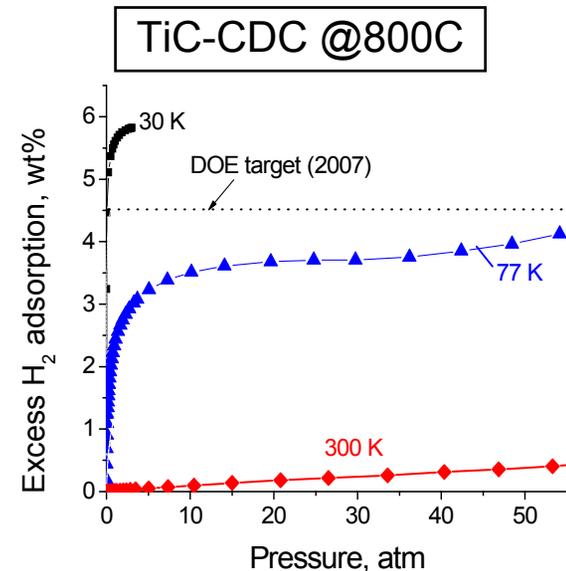
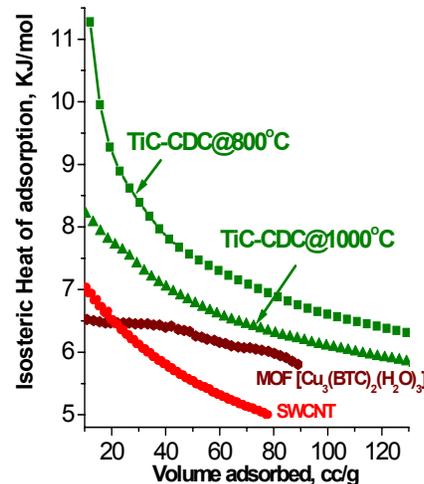
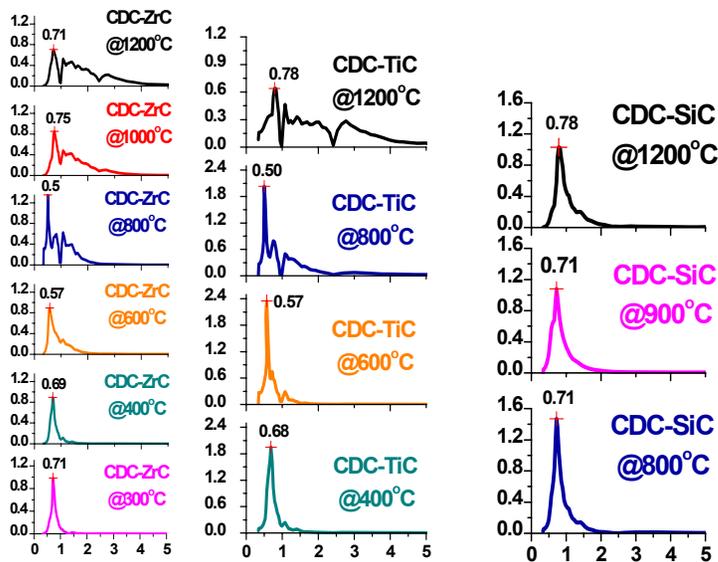
Cl_2
300 - 1200°C



- **May 2007:** ~ 50 different CDC materials synthesized and evaluated

Status May 2006

- Demonstrated tuneable SSA and PSD on ~30 distinct CDCs (below left).
- Proved that small pores are crucial for 1 atm storage.
- Highest SSA > 3000 m²/g (precursor: Ti₂AlC, chlorinated at 800°C).
- Heats of adsorption > carbon nanotubes, MOFs (below center).
- Highest gravimetric excess capacity 4.2% for NH₃-annealed TiC-CDC at 77K, 55 atm (below right).
- Initiated post-processing studies to achieve DOE targets with CDC.





Technical Accomplishments 2006 - 2007

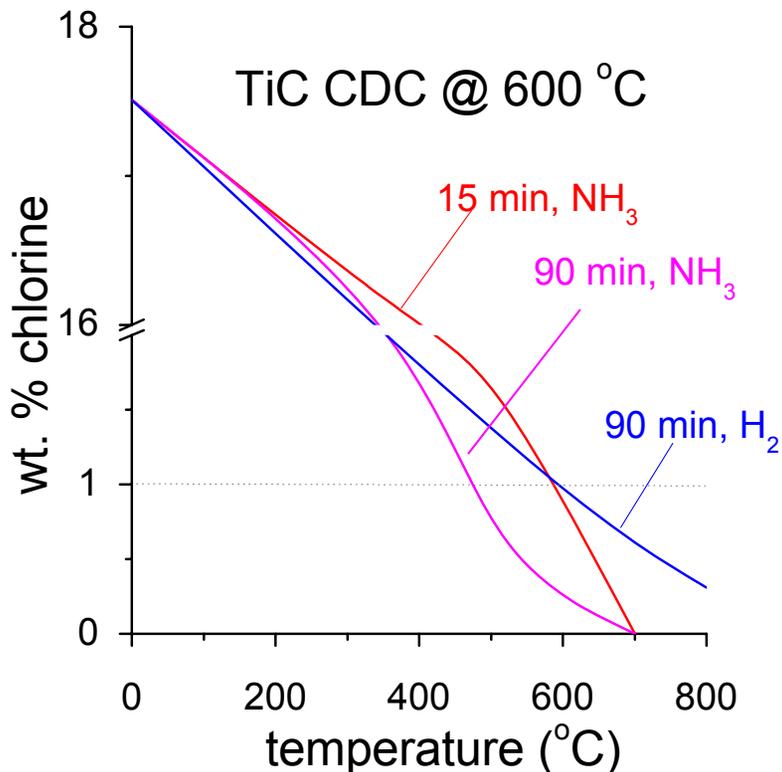
- Purification – remove elements blocking access to pores and/or plugging the pores – hydrogen vs. NH_3 .
- Activation – increase SSA by removing loosely bound carbon – motivated and guided by extensive literature on activated carbons.
- Chemical modification of pore (interior) surfaces to increase ΔH .
- Doping to increase ΔH : 3-center orbital overlaps (H, C, M); Kubas interaction.
- Improve volumetric capacity by compressing CDC powders.
- Nanoscale precursor carbides – chlorine reactions with undercoordinated metals/metalloids? More uniform product? Faster kinetics?

purification

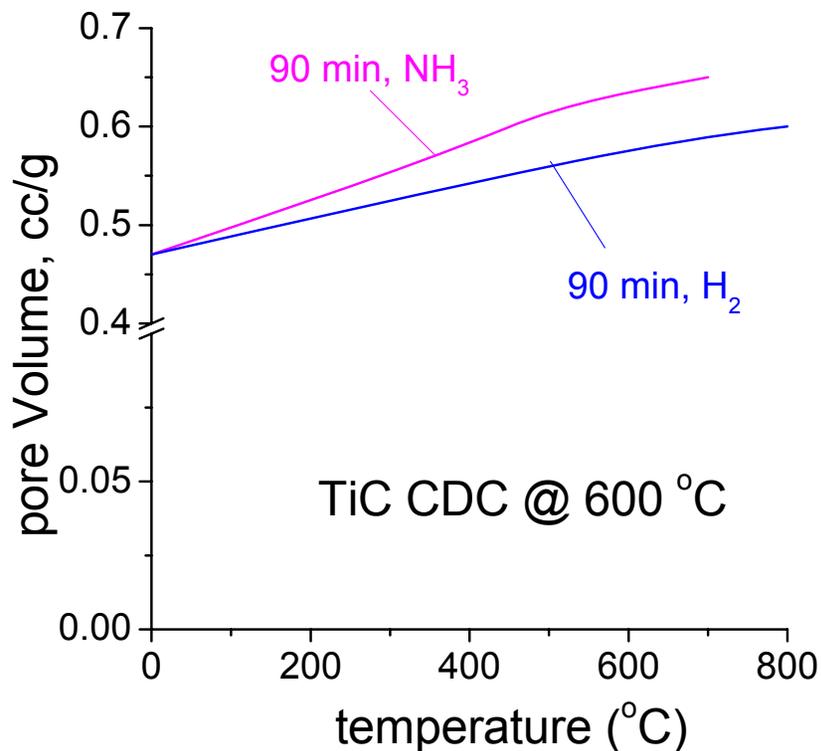
Hydrogen and ammonia post-treatments of CDC

- Chlorination leaves behind significant metals, chlorine, chlorides, ...
- These can be removed by annealing in flowing H_2 or NH_3 .
- Optimized annealing protocol combined with chlorination synthesis into a unified in-line process.

Cl_2 reduced from 17.5 wt% to < 1 wt%

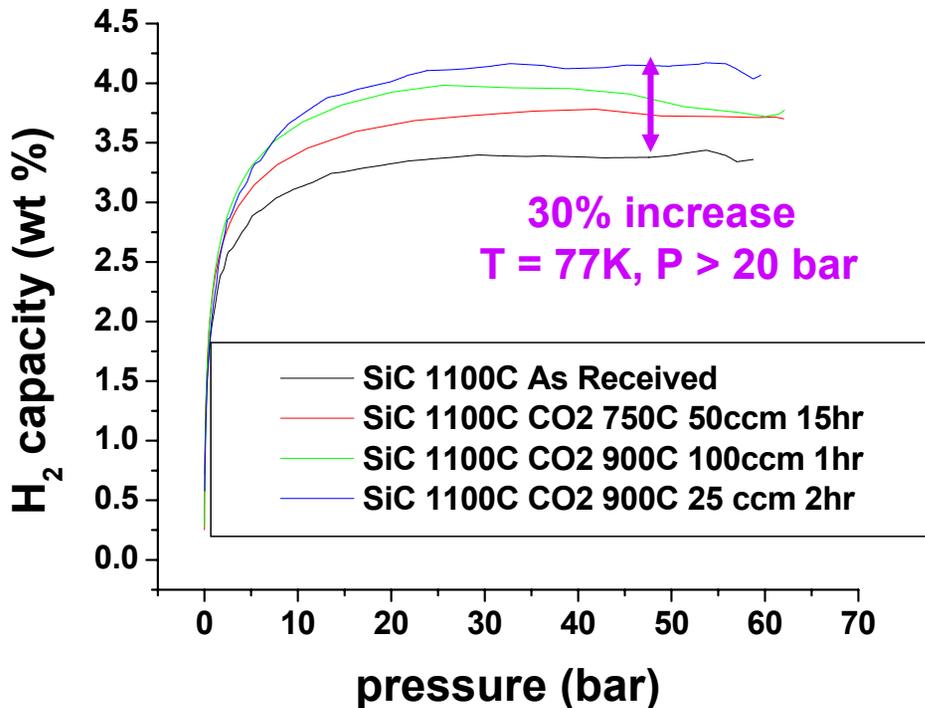


pore volume increases 30%

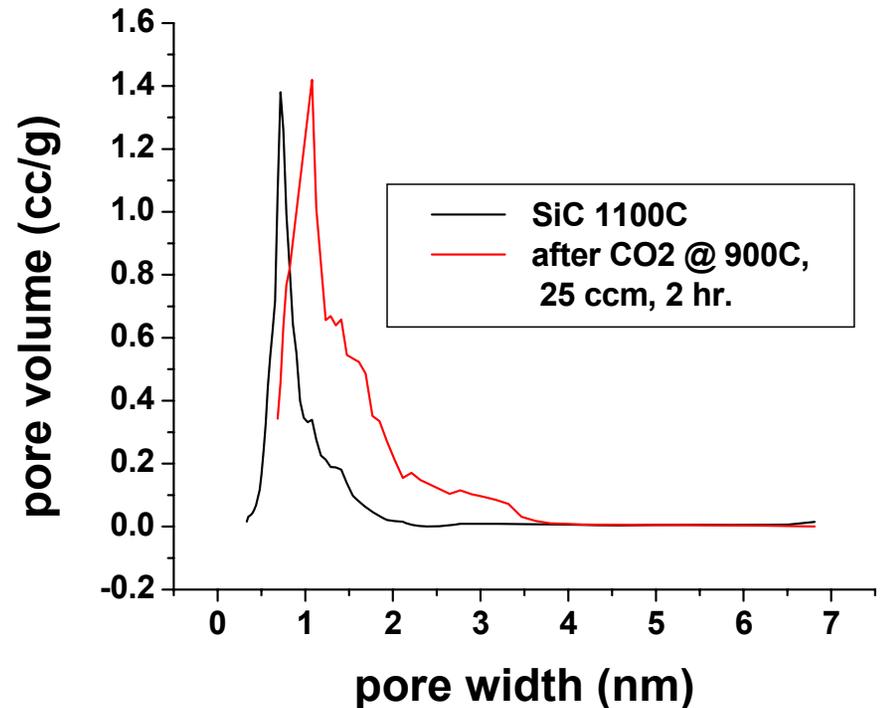


CO₂ activation

- We obtained promising results with CO₂ activation of SiC-derived CDC.
- Process optimized w.r.t. temperature, time and flowrate: 900C, 2 hr, 25 ccm.
- **BET SSA increases 65%** from 1424 to **2356 m²/gram**.
- **DFT pore volume increases 88%** from 0.52 to **0.98 cc/gram**.

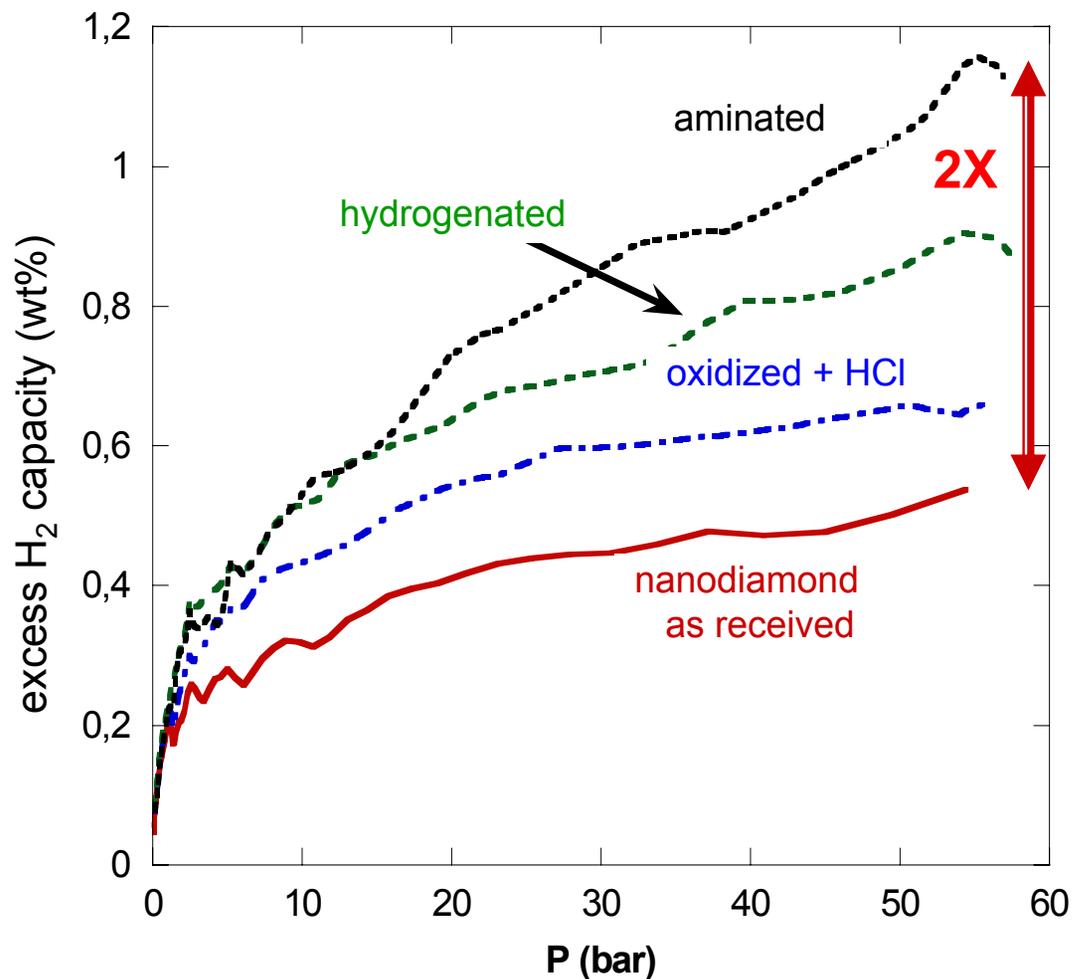


excess adsorption isotherms



pore size distribution

surface chemical modification: clues for CDC from nanodiamond studies

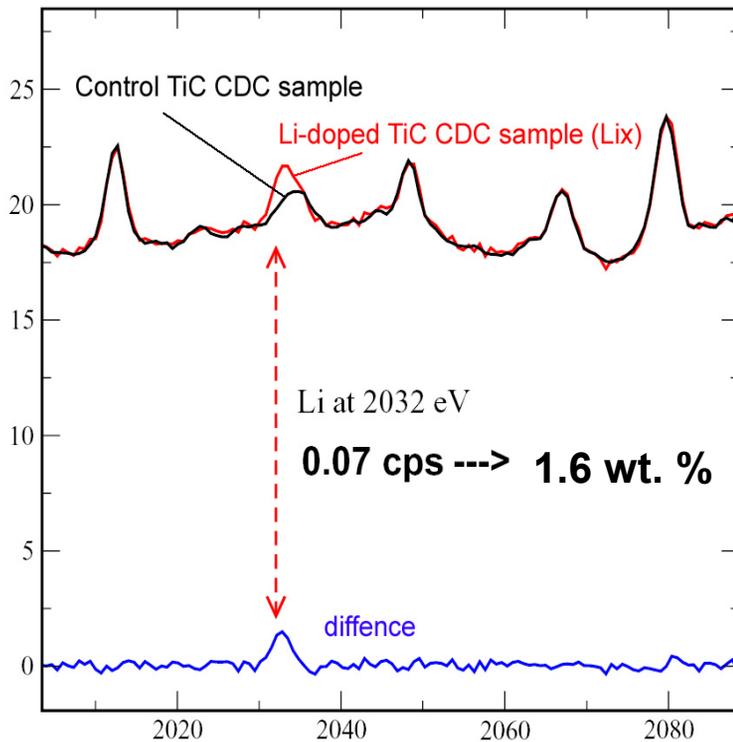


	SSA (m ² /g)	volume (cc/g)
pristine	287	0.182
air + HCl	316	0.199
H ₂	321	0.200
aminated	309	0.191

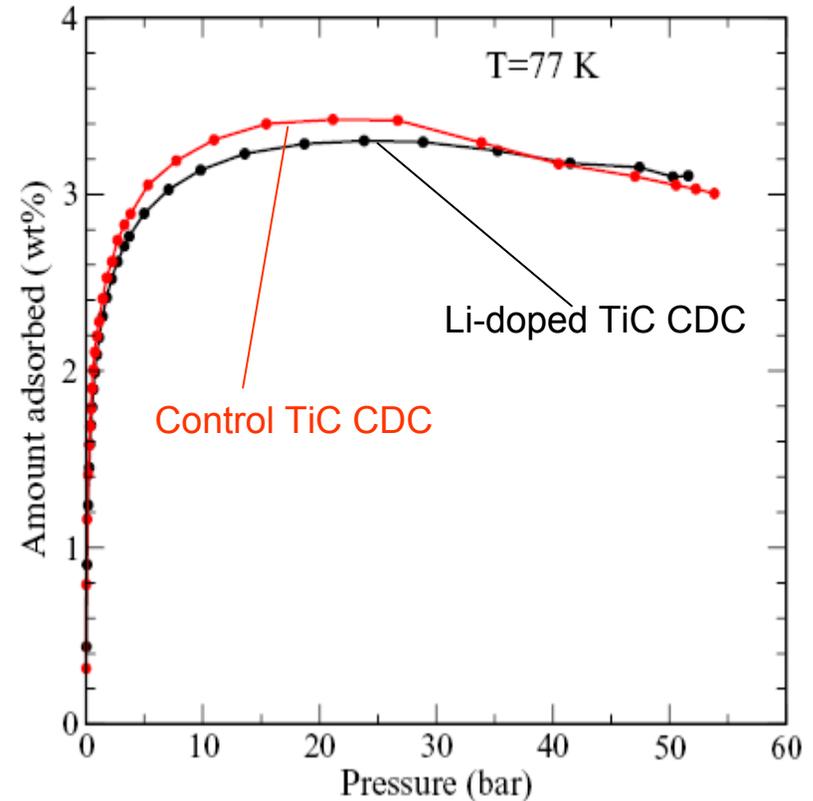
- Modified pore surface reactivity increases heat of adsorption.
- Only minimal effects on SSA and pore volume.
- May also apply to pore surfaces in CDC with large pores.

increase ΔH by doping: Li

Prompt Gamma-Ray Activation Analysis (PGAA)



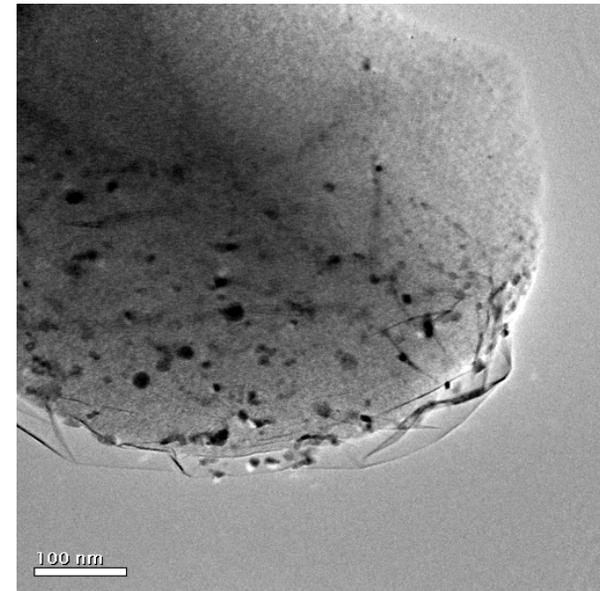
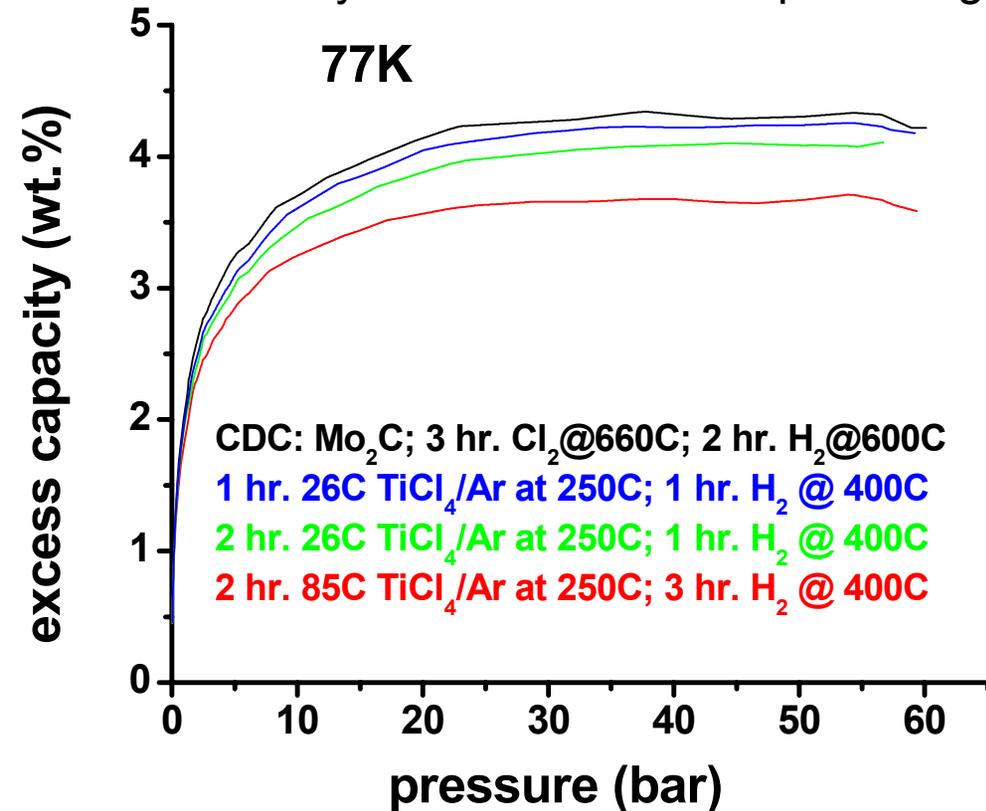
Excess Adsorption Isotherms



- Challenges: uniform doping, avoid oxidation, and avoid blocking pores with Li clusters.

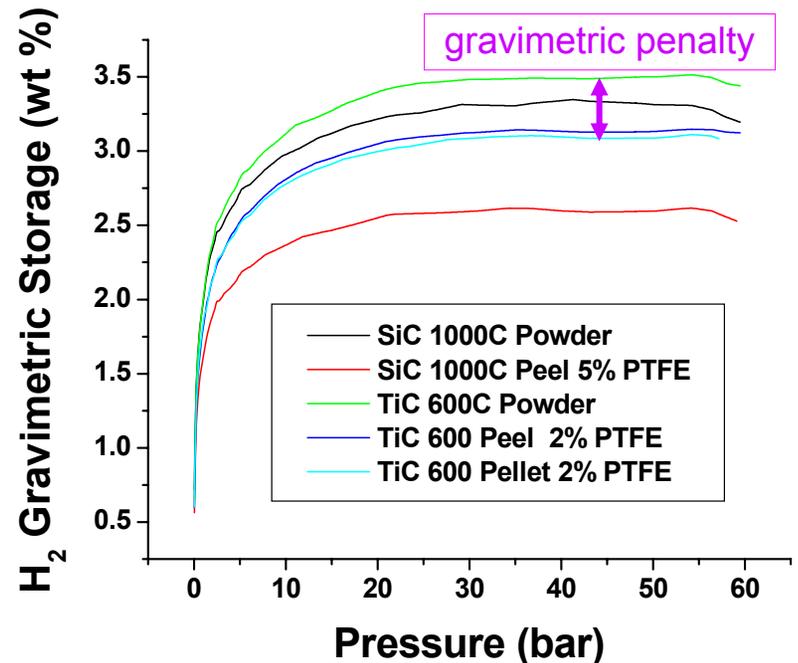
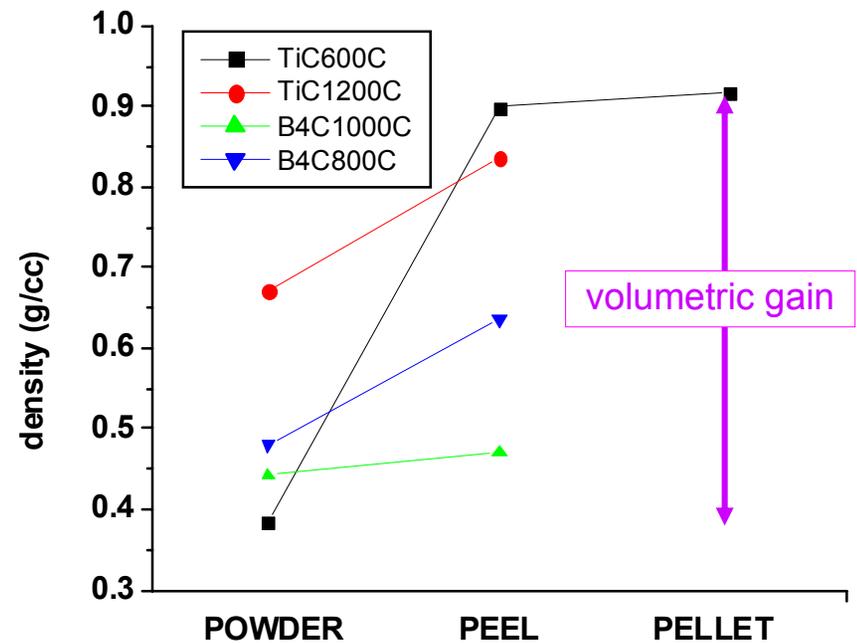
doping with Ti

- First, we need to develop new CDC with large pores and pore volume for *in situ* decomposition of Ti compounds - **Mo₂C-CDC @ 660°C; H₂-annealed at 600°C.**
- Even without doping, excess gravimetric capacity 4.2 wt% at 77K, P > 30 atm.
- TEM shows Ti-containing nanocrystals on the surface of Mo₂C-CDC particles.
- TGA in air: 7 wt% ash @ 1000C, identified as TiO₂ by XRD → 1.1 at% Ti.
- Preliminary Sieverts isotherms promising for enhanced ΔH .



improving the volumetric capacity of CDC powders

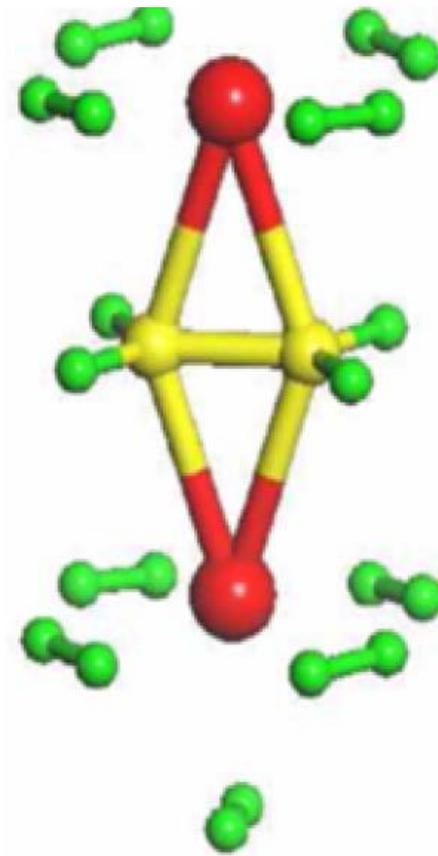
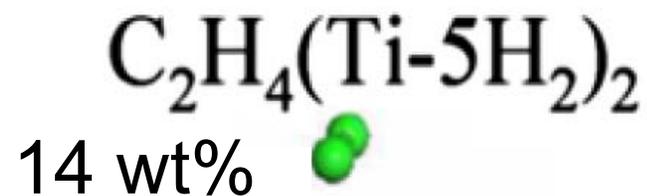
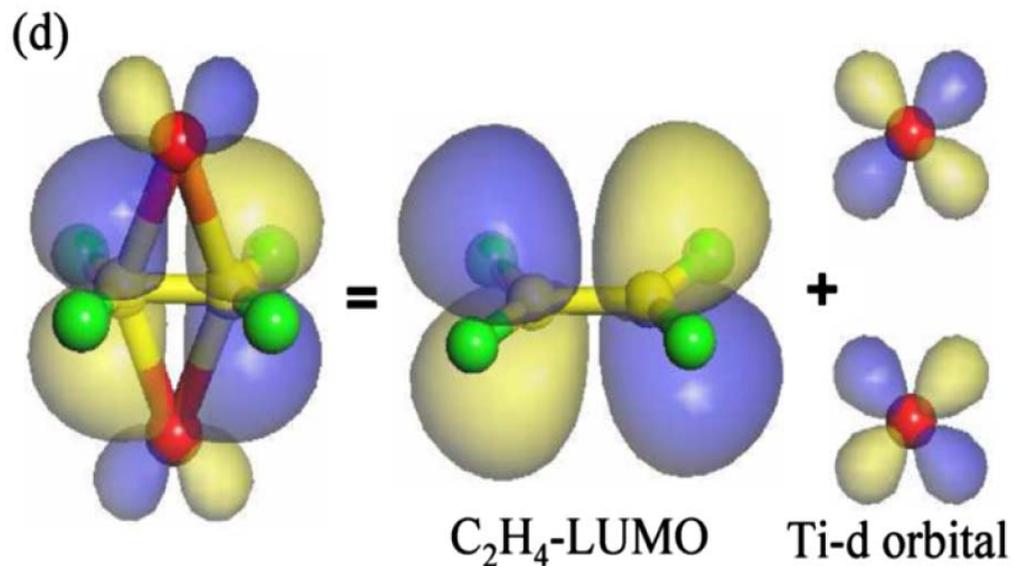
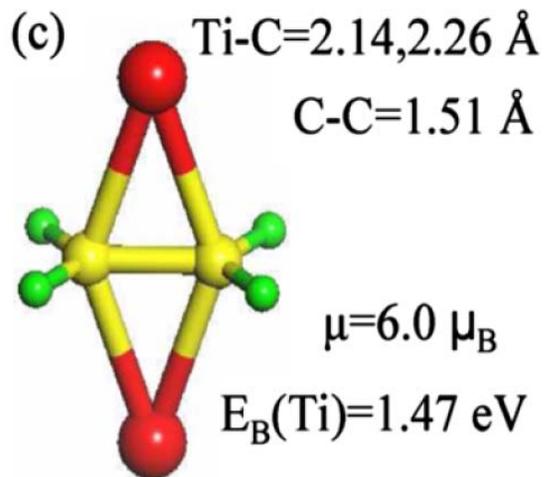
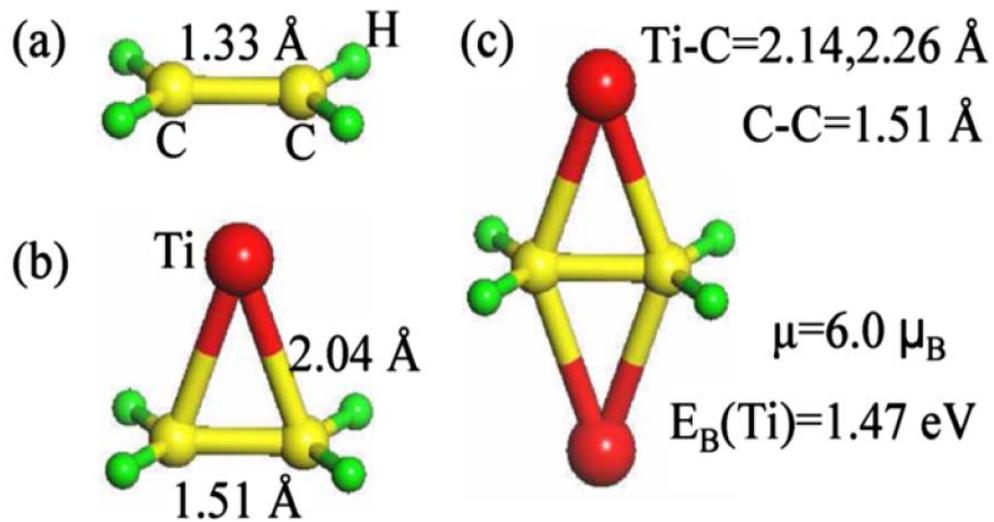
- Rolling peels with PTFE binder, similar to Li ion battery electrodes.
- Volumetric capacity increases by up to 100%, with 10-30% loss of gravimetric capacity which can be reduced by minimizing PTFE content. Need to correlate densification results with other properties.
- Density can be further increased by pressing stacks of peel disks into pellets. Correlate kinetics with densification.
- Advantages of powder can still be exploited, such as ease of uniform chlorination and chemical treatments.
- We will study an alternative – large stackable CDC particles, e.g. few mm cubes.





a challenge: modeling the pores in amorphous carbon

- Ab initio? Presently impossible to build a practicable structural model for top-down approaches; no periodicity.
- Independent slit pores? There is no experimental evidence for a significant volume fraction of interlayer correlations in H₂-optimized CDC. Furthermore, ΔH at low coverage \sim 2-3 times greater than calculated for slit pores.
- “Bottom-up” strategy: CDC comprised of sp² carbons (XANES, radial distribution function) connected in rings (reverse Monte Carlo), similar to 1970’s models of α -Si. Ring statistics specify the local atomic structure out to 3-4 neighbors.
- Simple surrogate – ethylene, including doped molecules such as **C₂H₄(TiH₂)₂** to which 5 H₂’s bind with 0.45 eV.



Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media



Plans for FY08 (i)

- Push towards 300K operation by **increasing the heat of adsorption**. Exploit metal-hydrogen interactions in a structurally-optimized system. CDC 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. Develop new approaches to remove amorphous carbon blocking pores and create additional small pores. Pore volumes up to 2 cm³/g and SSA of up to 4000 m²/g to be achieved.
- **Direct measurements of gravimetric capacity** on pelletized CDC powders and CDC plates produced from sintered ceramics. Find critical density/plate thickness at which we start losing capacity due to 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**.



Plans for FY08 (ii)

- Systematic study of novel routes to **achieve uniform dispersion of metal atoms** into carbon (CDC) network. Find strategies to avoid crystal growth, and to “prepare” sites for metal atom incorporation at the edges of bent graphene planes.
- Systematic study of mechanisms of carbon oxidation on the atomic scale. Find strategies to selectively and uniformly remove part of the carbon atoms from the porous and disordered carbon network, and to create point defects within the graphene layers that would further increase the surface area.
- Demonstrate large-scale (pounds) manufacturing of CDC and license the technology to a chemical company.



Project Summary

Relevance: Improvements in gravimetric and volumetric capacity were realized by processes which increase pore volume, heat of adsorption and powder density. Volumetric capacity was more than doubled by rolling peels with PTFE binder and pellet pressing. Even larger gains may be achieved with bulk precursors.

Approach: A suite of post-processing strategies were developed and optimized for specific precursors.

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

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

Prof. John E. Fischer
fischer@seas.upenn.edu
(215) 898-6924

Storage performance summary

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

storage parameter	units	2010 system target	FY06 materials**	FY07 result
specific energy density	kWh/kg (wt. % H ₂)	2.0 (6 wt.%)	4.3 wt%	4.5%
volumetric energy capacity	kWh/L (g/L)	1.5 45	34 (ideal)	22 (expt)

carbide	structure	ρ (carbide) (g/cm ³)	ρ (CDC) (ideal)	% pore volume
TiC	cubic	4.92	0.98	56.3
β -SiC	cubic	3.21	0.96	57.2
Ti ₃ SiC ₂ (312)	hex.	4.5	0.55	75.5
Cr ₄ C	cubic	6.99	0.38	83.1