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Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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Presentation for *Department of Energy: Hydrogen Storage Merit Review* on May 14-17, 2007.

Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

Abstract

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 H_2 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 H_2 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 H_2uptake.

Comments

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Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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Project ID:
ST-09

Objectives

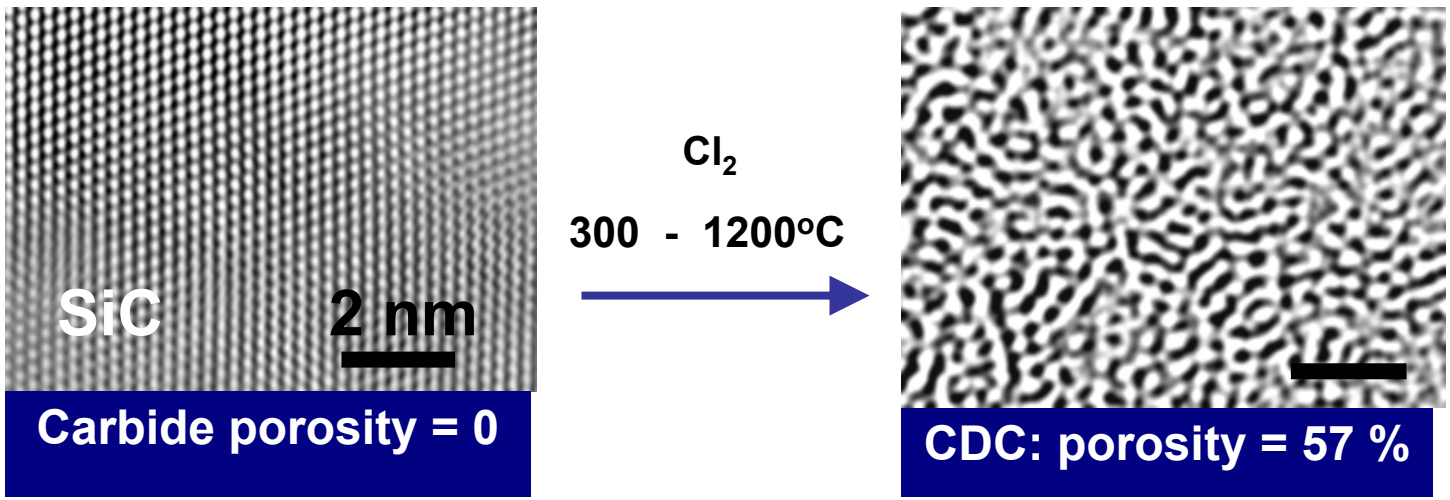
- Develop and demonstrate efficient, durable and reversible hydrogen storage in carbide-derived carbons (CDC) with tunable nanoporosity (2004-2005).
- Determine the optimum pore size for hydrogen storage using experiment and theory (2005-2006).
- Identify post-processing strategies and catalytic additives which maximize the performance of CDC-based hydrogen storage materials, using experiment and theory (2006-2007).
- Finalize the design of a CDC-based H_2 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: $MC + (1/2)Cl_2 \rightarrow MCl(gas) + C$,

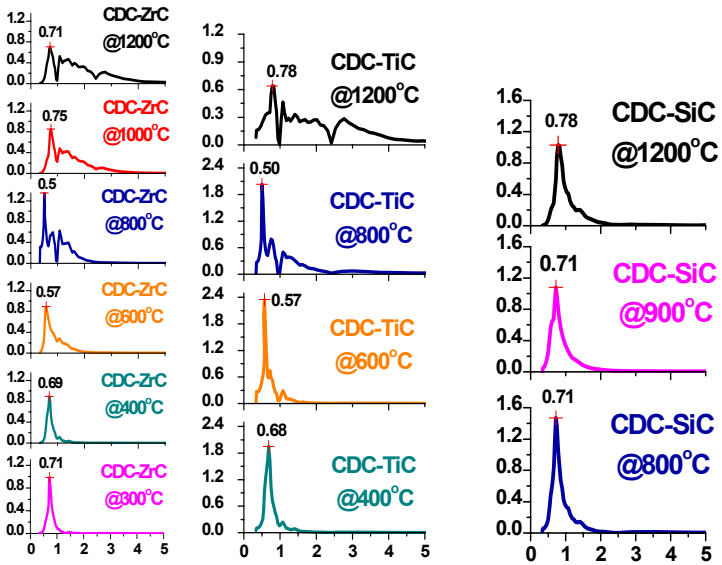
M = metal or metalloid
C = carbide-derived carbon

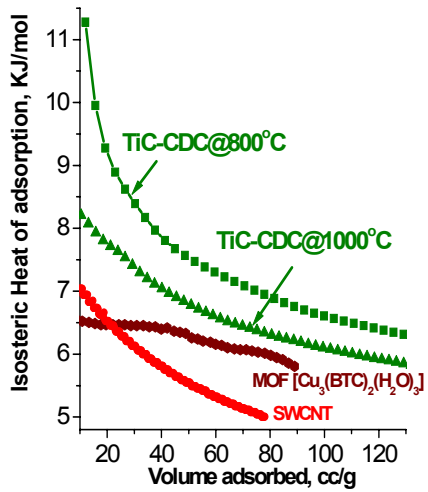


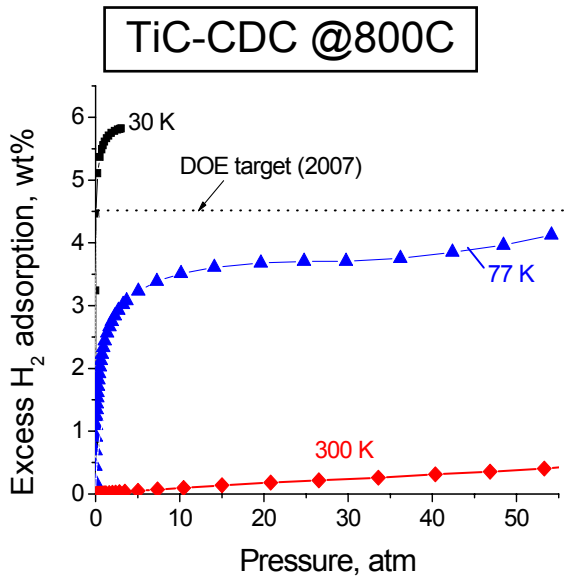
- **May 2007**: ~ 50 different CDC materials synthesized and evaluated

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 m^2/g (precursor: Ti_2AlC, chlorinated at 800°C).
- Heats of adsorption > carbon nanotubes, MOFs (below center).
- Highest gravimetric *excess* capacity 4.2% for NH_3–annealed TiC-CDC at 77K, 55 atm (below right).
- Initiated post-processing studies to achieve DOE targets with CDC.







Technical Accomplishments 2006 - 2007

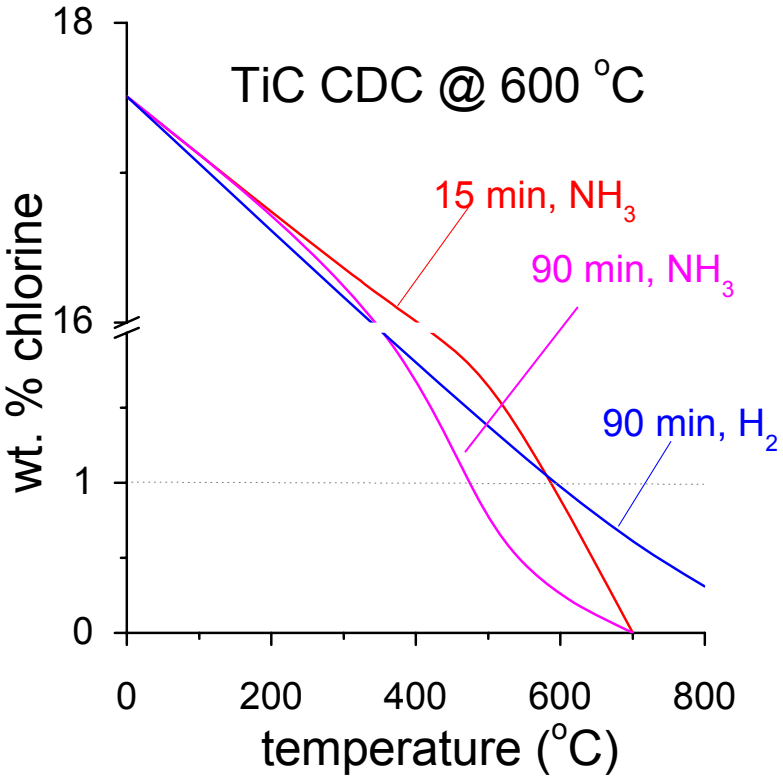
- Purification – remove elements blocking access to pores and/or plugging the pores – hydrogen *vs.* NH_3.
- Activation – increase SSA by removing loosely bound carbon – motivated and guided by extensive literature on activated carbons.
- Chemical modification of pore (interior) surfaces to increase *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

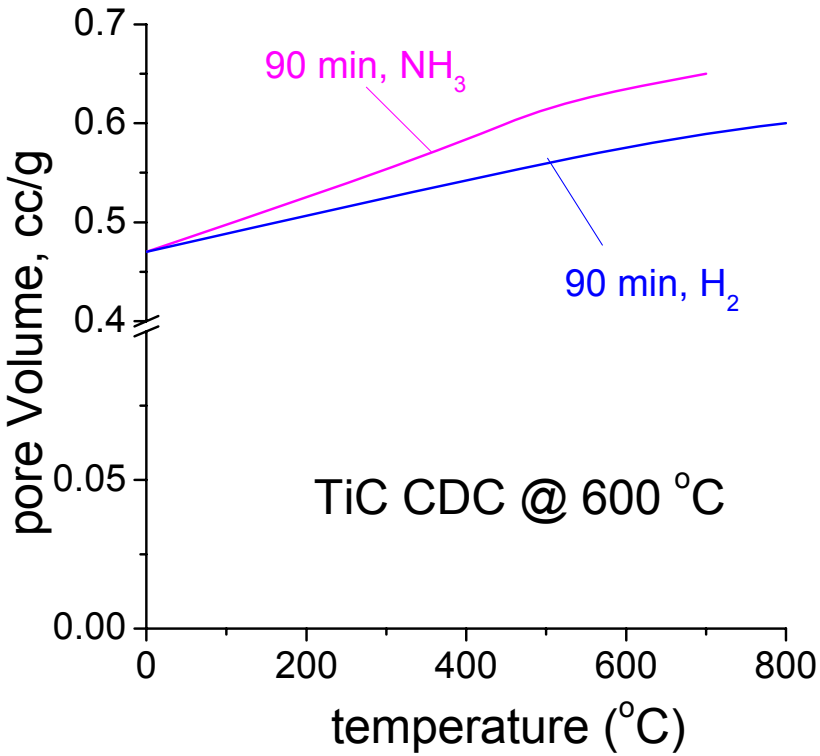
Hydrogen and ammonia post-treatments of CDC

- **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%

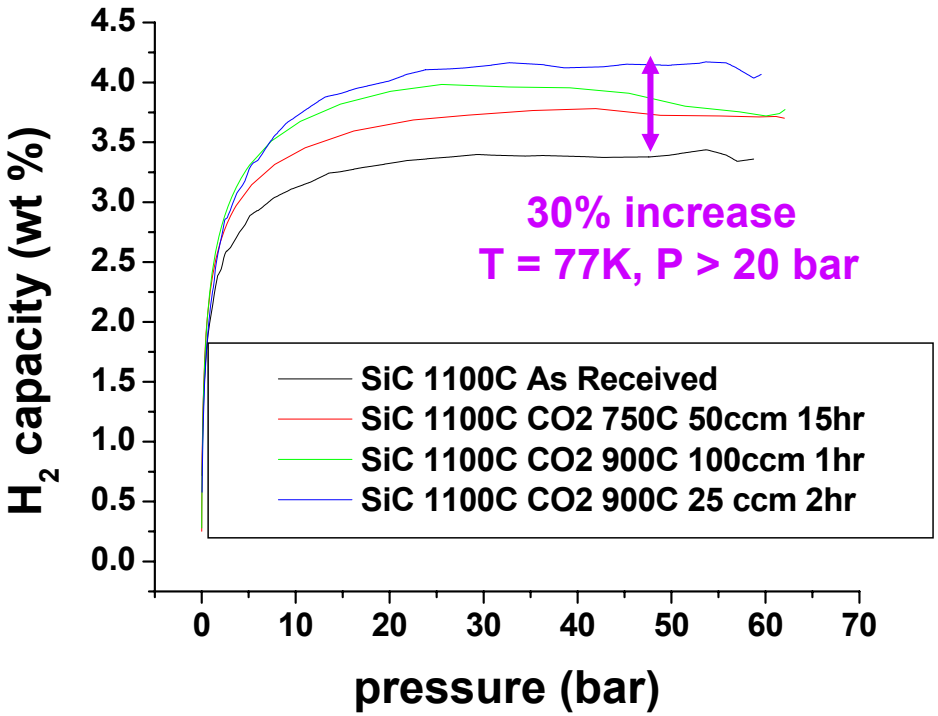


pore volume increases 30%

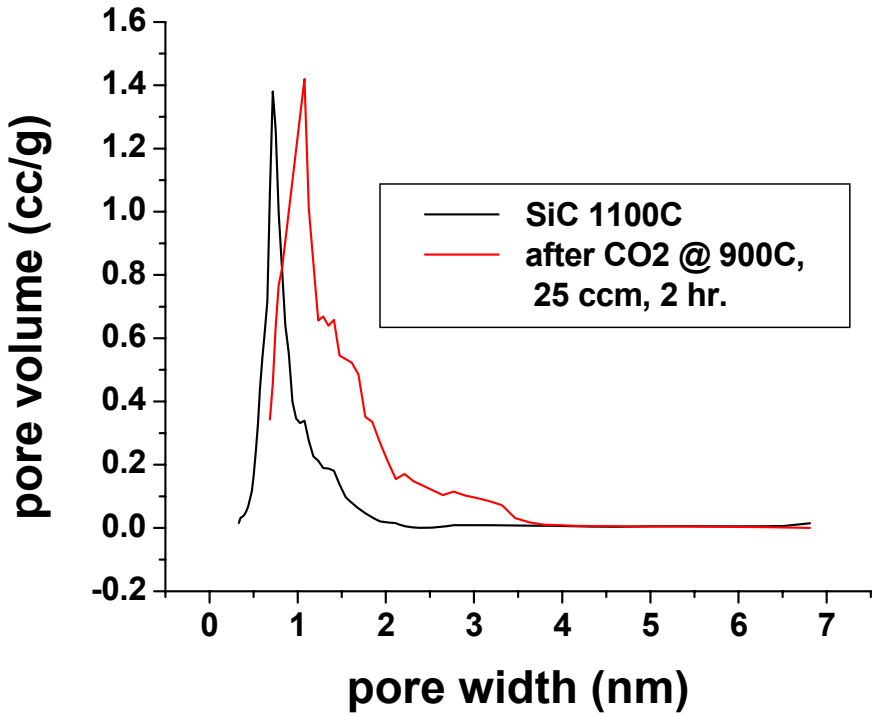


CO_2 activation

- We obtained promising results with CO_2 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 m^2/gram.
- DFT pore volume increases 88% from 0.52 to 0.98 cc/gram.

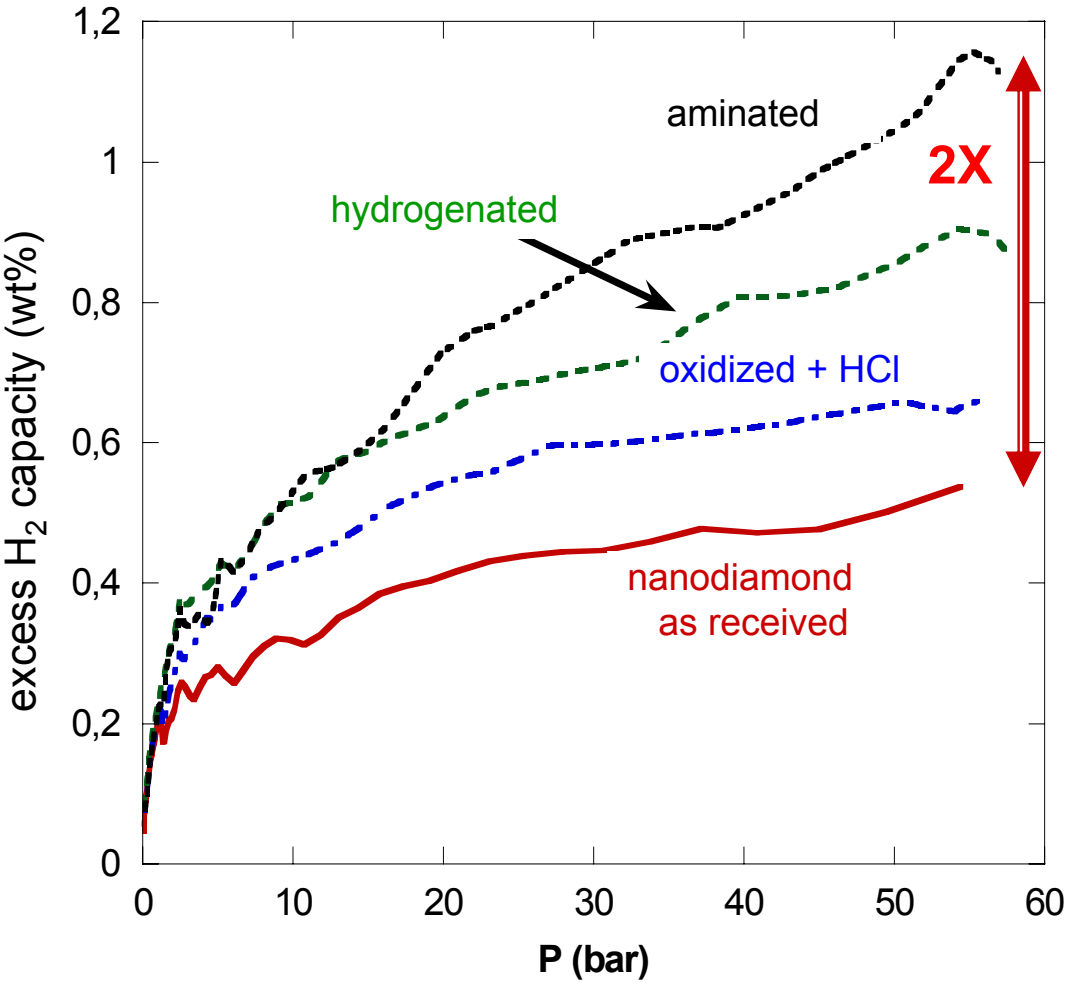


excess adsorption isotherms



pore size distribution

surface chemical modification: clues for CDC from nanodiamond studies

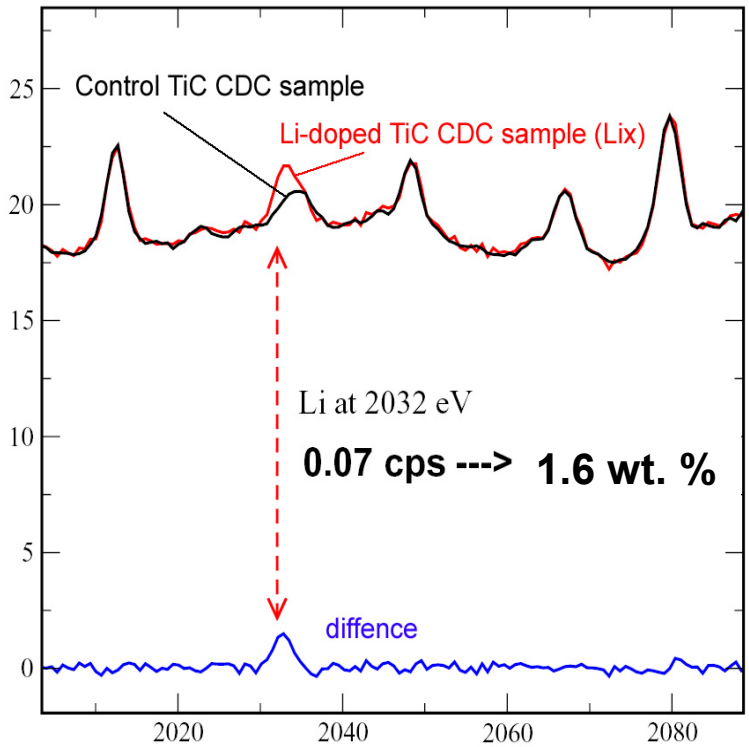


	SSA (m^2/g)	volume (cc/g)
pristine	287	0.182
air + HCl	316	0.199
H_2	321	0.200
aminated	309	0.191

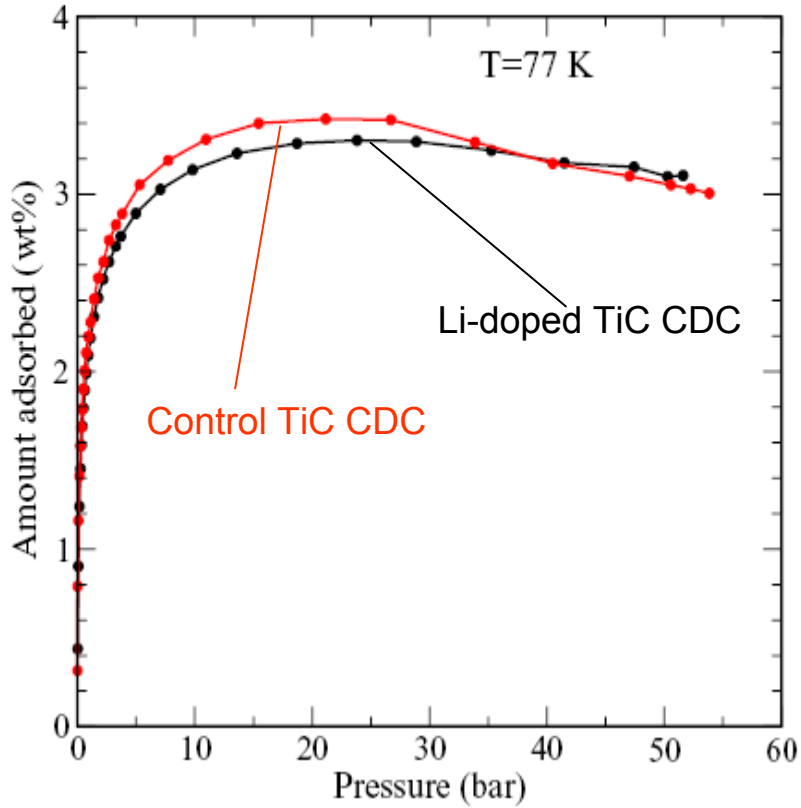
- Modified pore surface reactivity increases heat of adsorption.
- Only minimal effects on SSA and pore volume.
- May also apply to pore surfaces in CDC with large pores.

increase ΔH by doping: Li

Prompt Gamma-Ray Activation Analysis (PGAA)



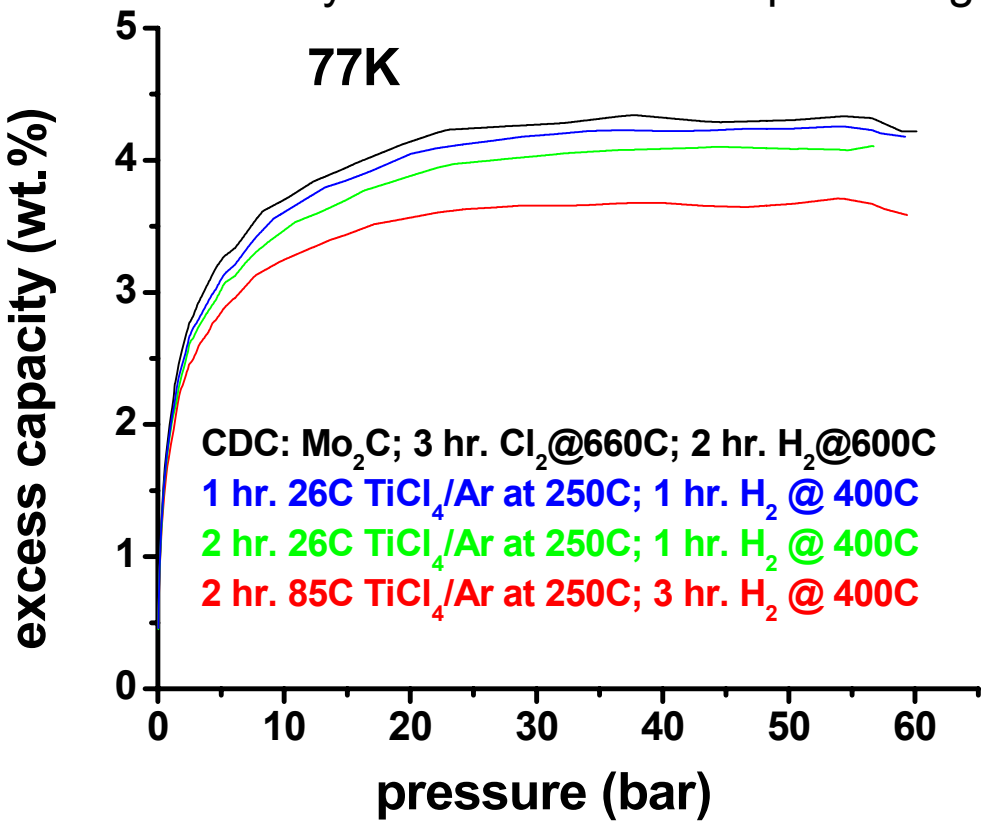
Excess Adsorption Isotherms

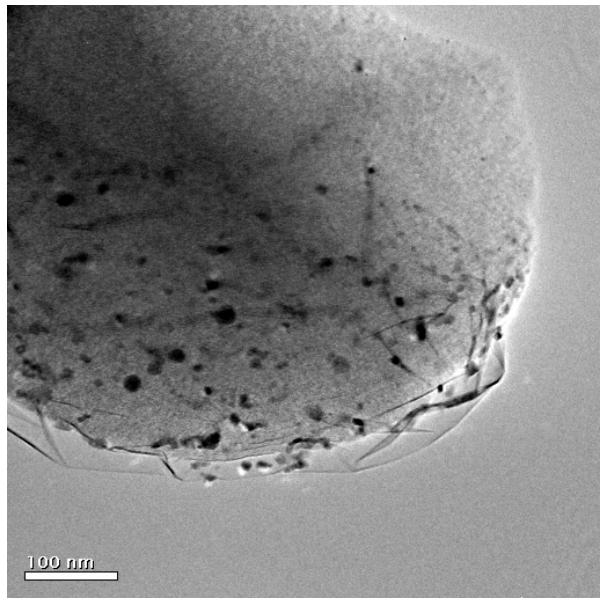


- Challenges: uniform doping, avoid oxidation, and avoid blocking pores with Li clusters.

doping with Ti

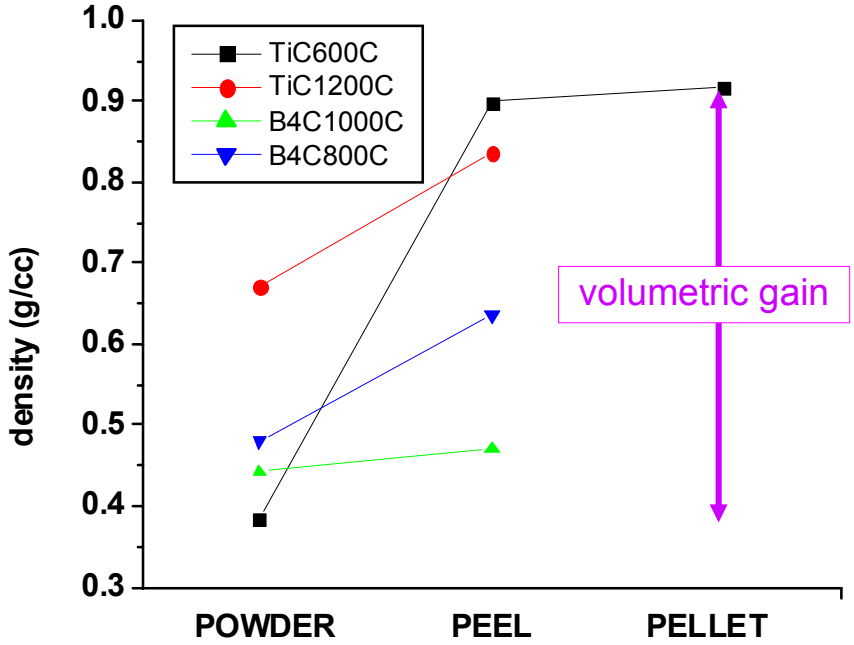
- First, we need to develop new CDC with large pores and pore volume for *in situ* decomposition of Ti compounds - **Mo_2C-CDC @ 660°C; H_2-annealed at 600°C.;** .
- Even without doping, e*xcess* gravimetric capacity 4.2 wt% at 77K, P > 30 atm.
- TEM shows Ti-containing nanocrystals on the surface of Mo2C-CDC particles.
- TGA in air: 7 wt% ash @ 1000C, identified as TiO_2 by XRD ➡ 1.1 at% Ti.
- Preliminary Sieverts isotherms promising for enhanced ΔH.

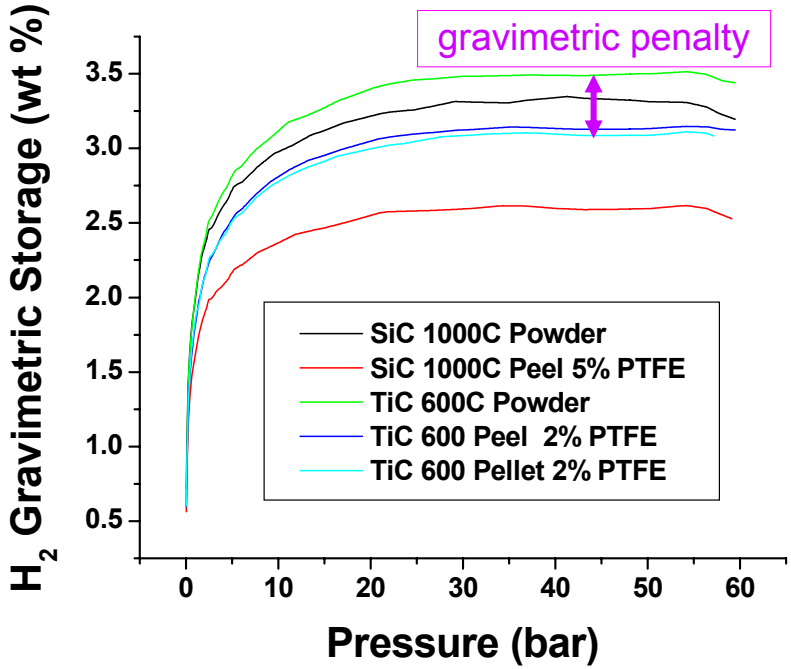




improving the volumetric capacity of CDC powders

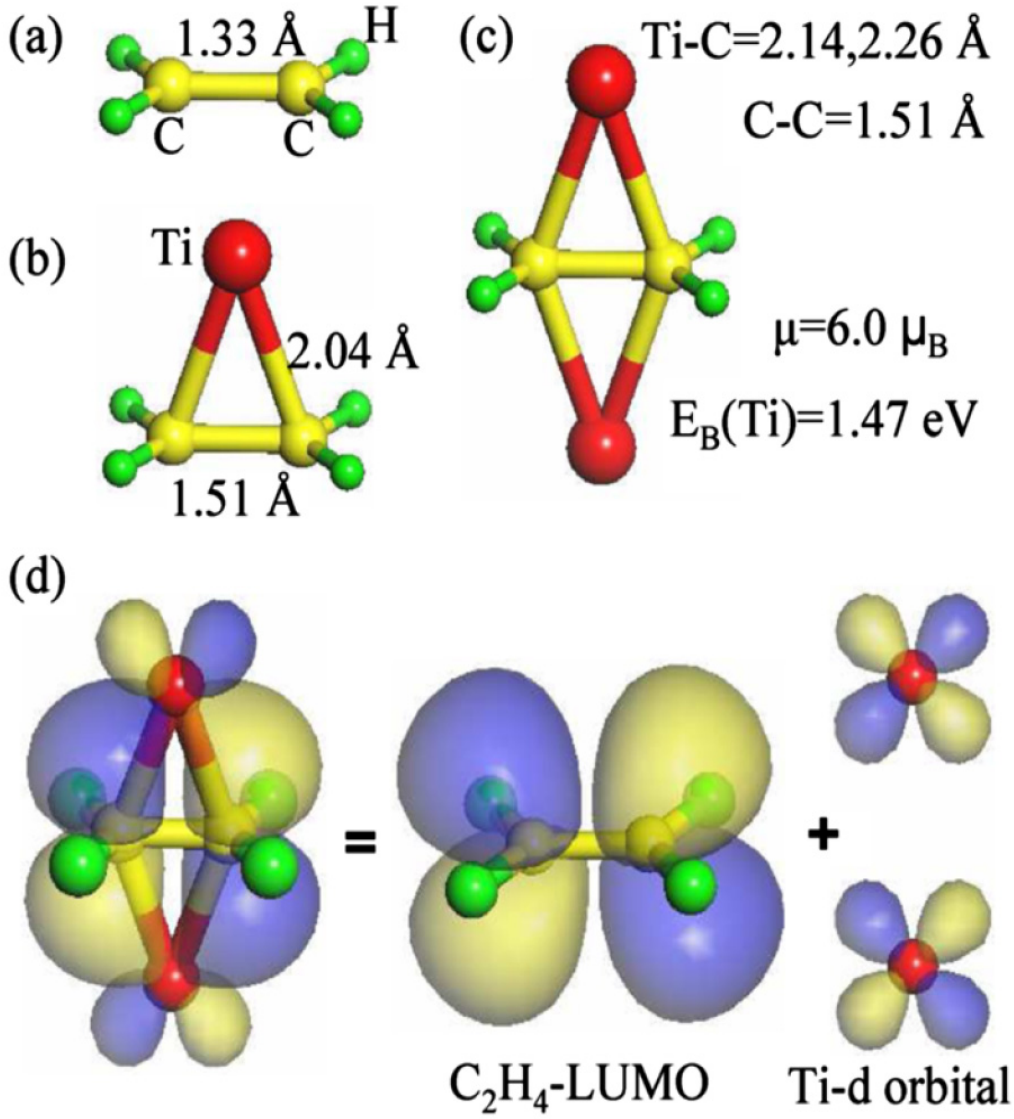
- Rolling peels with PTFE binder, similar to Li ion battery electrodes.
- Volumetric capacity increases by up to 100%, with 10-30% loss of gravimetric capacity which can be reduced by minimizing PTFE content. Need to correlate densification results with other properties.
- Density can be further increased 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.





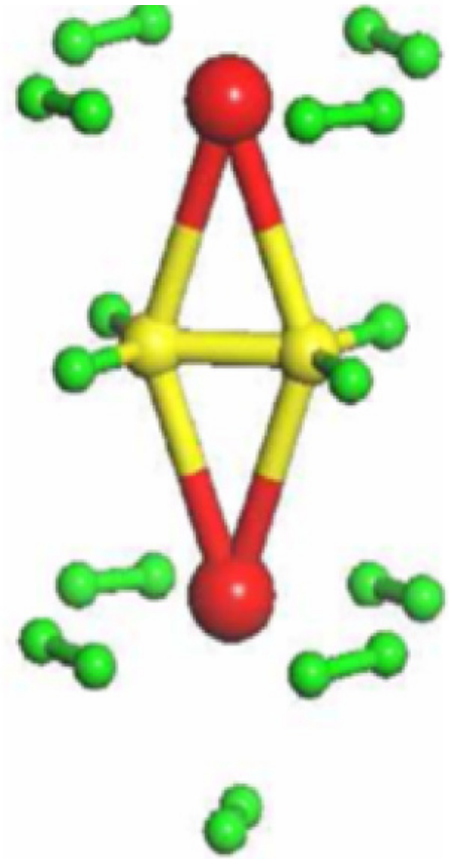
a challenge: modeling the pores in amorphous carbon

- *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 ~ 2-3 times greater than calculated for slit pores.
- *"Bottom-up" strategy*: CDC comprised of sp^2 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 $C_2H_4(TiH_2)_2$ to which 5 H_2's bind with 0.45 eV.



$C_2H_4(Ti\text{-}5H_2)_2$

14 wt%



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

E. Durgun,[1,2] S. Ciraci,[1,2,*] W. Zhou,[3,4] and T. Yildirim[3,4]

PRL **97,** 226102 (2006)

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Publications

1. Tailoring of Porosity in Carbide-Derived Carbons for Hydrogen Storage , Y. Gogotsi , R.K. Dash, G. Yushin, T. Yildirim, G. Laudisio, J.E. Fischer, ***J. Am. Chem. Soc.*** **127**, 16006-16007 (2005).
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4. Titanium Carbide-Derived Nanoporous Carbon for Energy-Related Applications, R.K. Dash, G. Yushin, G. Laudisio, J. Chmiola, J. E. Fischer, Y. Gogotsi, ***Carbon*** **44**, 2489-2497 (2006).
5. Design of Porous Carbon for Efficient Hydrogen Storage , G. Yushin, R.K. Dash, J. Jagiello, J. E. Fischer, Y. Gogotsi, ***Adv. Funct. Mat.*** **16**, 2288-2293 (2006).
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8. Hydrogen Absorption Properties of Metal-Ethylene Complexes, W. Zhou, and T. Yildirim, E. Durgun, S. Ciraci, ***Phys. Rev. B*** *(*submitted).

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3. Nanoporous Carbide Derived Carbon with Tunable Pore Size: Synthesis and Energy-Related Applications (invited); G. Yushin, J. Chmiola, R.K. Dash, E. Hoffman, M. Barsoum, Y. Gogotsi, G. Laudisio and **J. E. Fischer**, 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 (invited), Y. Gogotsi, R.K. Dash, G. Yushin, T. Yildirim, G. Laudisio and **J.E. Fischer**, Hydrogen Storage with Novel Materials, Bad Honnef, Germany, Oct 23-27, 2005.
5. **G. Yushin**, J. Chmiola, R. Dash, Y. Gogotsi, C. Portet, P. Simon, P.-L. Taberna, J. Fischer, R. Rest, Carbide Derived Carbon for Energy Related Applications, NASA Tech Briefs National Nano Engineering Conference, Boston, MA (2006).
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Presentations (cont'd.)

8. Tailored Nanoscale Porosity in Carbide-Derived Carbons: Optimization for High Capacity Hydrogen Storage (invited), R. K. Dash, G. Yushin, **Y. Gogotsi**, G. Laudisio, J. P. Singer and J. E. Fischer, International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara CA August 20-25, 2006.
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14. Hydrogen Absorption Properties of Metal-Ethylene Complexes, **W. Zhou**, and T. Yildirim, E. Durgun, S. Ciraci, NIST Sigma-Xi Postdoctoral Poster Presentation, Gaithersburg, MD. 2007.
15. Carbide-Derived Carbons for Energy-Related and Biomedical Applications (invited), **Y. Gogotsi**, From the Lab to the Marketplace: Nanotechnology Symposium, Polytechnic University, Brooklyn, NY, April 23, 2007.