Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

John E. Fischer¹,³, Yury Gogotsi², and Taner Yildirim³,¹

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

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

³National Institute of Standards and Technology
Gaithersburg, MD 20899

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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., 300-1200°C.
- **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: \[ \text{MC} + \frac{1}{2}\text{Cl}_2 \rightarrow \text{MCl}(\text{gas}) + \text{C}, \]

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 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. NH₃.
- 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.
Chlorination leaves behind significant metals, chlorine, chlorides, ...
These can be removed by annealing in flowing H₂ or NH₃.
Optimized annealing protocol combined with chlorination synthesis into a unified in-line process.

Cl₂ reduced from 17.5 wt% to < 1 wt%

pore volume increases 30%
We obtained promising results with CO$_2$ activation of SiC-derived CDC. Process optimized w.r.t. temperature, time and flowrate: 900°C, 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.

**CO$_2$ activation**

- **30% increase**
  - $T = 77$K, $P > 20$ bar

**Graphs:**
- Excess adsorption isotherms
- Pore size distribution

**Legend:**
- SiC 1100C As Received
- SiC 1100C CO$_2$ 750°C 50ccm 15hr
- SiC 1100C CO$_2$ 900°C 100ccm 1hr
- SiC 1100C CO$_2$ 900°C 25 ccm 2hr
surface chemical modification: clues for CDC from nanodiamond studies

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m²/g)</th>
<th>Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>287</td>
<td>0.182</td>
</tr>
<tr>
<td>air + HCl</td>
<td>316</td>
<td>0.199</td>
</tr>
<tr>
<td>H₂</td>
<td>321</td>
<td>0.200</td>
</tr>
<tr>
<td>aminated</td>
<td>309</td>
<td>0.191</td>
</tr>
</tbody>
</table>

Graph showing:
- Excess H₂ capacity (wt%)
- P (bar)
- SSA and volume values for different samples:
  - nanodiamond as received
  - hydrogenated
  - oxidized + HCl
  - aminated
increase $\Delta H$ by doping: Li

Promt Gamma-Ray Activation Analysis (PGAA)

- Control TiC CDC sample
- Li-doped TiC CDC sample (Li$_x$)
- Li at 2032 eV
- 0.07 cps $\rightarrow$ 1.6 wt. %

Excess Adsorption Isotherms

- T=77 K
- Li-doped TiC CDC
- Control TiC CDC

• Challenges: uniform doping, avoid oxidation, and avoid blocking pores with Li clusters.
First, we need to develop new CDC with large pores and pore volume for \textit{in situ} decomposition of Ti compounds - Mo$_2$C-CDC @ 660°C; H$_2$-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 @ 1000°C, identified as TiO$_2$ by XRD 1.1 at% Ti.
- Preliminary Sieverts isotherms promising for enhanced $\Delta H$.

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77K
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```
excess capacity (wt.%) 0 1 2 3 4 5
pressure (bar) 0 10 20 30 40 50 60
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CDC: Mo$_2$C; 3 hr. Cl$_2$ @ 660°C; 2 hr. H$_2$ @ 600°C
1 hr. 26°C TiCl$_4$/Ar at 250°C; 1 hr. H$_2$ @ 400°C
2 hr. 26°C TiCl$_4$/Ar at 250°C; 1 hr. H$_2$ @ 400°C
2 hr. 85°C TiCl$_4$/Ar at 250°C; 3 hr. H$_2$ @ 400°C
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, $\Delta H$ 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 $\alpha$-Si. Ring statistics specify the local atomic structure out to 3-4 neighbors.

- **Simple surrogate – ethylene**, including doped molecules such as $\text{C}_2\text{H}_4(\text{TiH}_2)_2$ to which 5 H$_2$’s bind with 0.45 eV.
Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media

E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim

PRL 97, 226102 (2006)
**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$_2$ uptake.

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


Presentations


Presentations (cont’d.)


