Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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Overview

Timeline
- **Project start:** Oct 2004
- **Project end:** Sept 2008
- 85% complete

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.

Budget
- **Total project funding** (expected)
  - DOE - $1,440,488 K
  - Contractor - $370 K
- **Funding received in FY07**
  - $325 K
- **Funding for FY08**
  - $456,488 K
  - no-cost extension likely

Collaborations
- Prof. A. Linares-Solano (Spain) – KOH activation
- Ioffe Institute (Russia) CDC samples
- Profs. K. Gubbins (UNC), M. Kertesz (Georgetown), Dr. Anna Llobet (LANSCE/LANL) – local structure
- NIST – inelastic neutron scattering; PGAA analysis for carbon purity.
- Y-Carbon – license for material manufacturing, will scale up the process
Objectives and Milestones

- Demonstrate that CDC powders can be compacted by rolling or pellet pressing to restore volumetric capacity without degrading gravimetric capacity (2007).
- Establish database for >50 distinct CDC materials made and measured to date (2007).
- Identify post-processing strategies which maximize the performance of CDC-based hydrogen storage materials (2006-2008).
- Create a structural model for pores in CDC based on neutron scattering and hybrid reverse Monte Carlo analysis; learn from theory and modeling if these represent equilibrium atomic configurations and how they control sorption behavior (2005-2008).
- Finalize the design of a CDC-based H₂ storage material that meets 2010 DOE performance targets (2007-2008).
Approach

Synthesize “designer” pore structures in amorphous carbon by leaching metals out of crystalline metal carbides using chlorine at ~1 atm., 300-1200°C.

Optimize pore size, shape, size distribution, SSA and total volume by choice of precursor (crystal symmetry, M/C ratio, and synthesis conditions (chlorination temperature, time, flow rate).

“ACTIVATION”
Increases SSA and total pore volume in many carbons. We know that pores < 1 nm dominate H₂ sorption in CDC’s; what do PSD’s look like after activation?

SURFACE TREATMENT
Use nanodiamond as an “inside-out” surrogate for porous carbon – low SSA but surfaces completely accessible. H₂ Sieverts and SSA measurements after exposure to gases.

DOPING (Li, K, Ti, Ni)
Develop atom-scale metal center interactions (not catalysis) to enhance H₂ binding with carbon network - e.g. Dewar/Kubas d-orbital hybridization – avoid forming nanoclusters, blocking pores.

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.

purify/anneal in H₂ or NH₃

Characterization: Raman, TEM, EDS, WAXS and PGAA for purity and state of the carbon network;
Performance: sorption with various gases (SSA, PSD’s etc), H₂ isotherms 30-300K and 1-50 atm.; SAXS
Chemical activation with KOH (Alicante)

A one-step process with high yield (low burnoff) > 60%. Produces large increase in micropore volume and SSA, with controlled narrow PSD’s.

Activation is effective for any chlorination temperature; as we previously found out, 1000°C is too high due to the onset of graphitization.

KOH activation of TiC-derived CDC increases SSA by as much as a factor 2, yielding 70-80% porosity.
KOH activation increases pore volume preferentially via micropores at low chlorination temperatures. PSD’s (not shown) reveal that KOH also increases the volume of larger pores, and also the average pore size.

KOH increases gravimetric capacity by up to 44%, dominated by increased volume of pores < 1.5 nm.
Physical activation with CO$_2$

TiC-CDC @ 600°C

- CO$_2$ is a milder oxidant than air but higher burn-off (lower yield) than KOH.
- 50% yield at 875°C; decreases notably at higher CO$_2$ temperatures.
- 8 hrs required to saturate the process at 875 °C.
- At fixed 2 hr time, SSA and pore volume increase linearly with increasing T(CO$_2$).

CO$_2$ increases SSA and pore volume by up to 130%.
Effect on $H_2$ storage: a tradeoff between SSA and micropore volume

**CO$_2$-activated TiC@600C**

60 bars, 77K

**0°C isotherm w/CO$_2$**

<table>
<thead>
<tr>
<th>Activation temperature ($°C$)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.40</td>
</tr>
<tr>
<td>850</td>
<td>0.45</td>
</tr>
<tr>
<td>900</td>
<td>0.50</td>
</tr>
<tr>
<td>950</td>
<td>0.55</td>
</tr>
<tr>
<td>1000</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Excess $H_2$ capacity (wt%)

- control
- CO$_2$ act 875°C, 2h
- CO$_2$ act 875°C, 6h
- CO$_2$ act 875°C, 8h
- CO$_2$ act 900°C, 2h
- CO$_2$ act 930°C, 2h
- CO$_2$ act 950°C, 2h

Micropore volume (pores<1.5nm) (cc/g)

- control
- 1h
- 2h
- 4h
- 6h
- 8h
- 12h

Up to 50% enhancement of gravimetric capacity, either with SSA > 3000 and some large pores (950°C, 2 hr.), or SSA = 2700 and no large pores (875°C, 8 hr.)
H₂ storage in CO₂ - activated SiC-CDC

Without activation, purified SiC-CDC underperform their TiC counterparts because the volume of pores < 1 nm. is smaller. Optimized CO₂ activation brings SiC-CDC performance into the range of activated TiC-CDC.

Any CDC which shows increased micropore volume after activation will show significantly enhanced H₂ capacity.
Overall, linear dependence of storage on BET SSA, similar to 1 atm.  Similar to 1 atm., small pores are overweighted in the SSA/normalized storage.

Activation is maximally effective if the increase in SSA comes mainly from small pores. On this basis, CDC’s can outperform AC’s.
Surface chemical modification: clues for CDC from nanodiamond studies

- Surfaces completely accessible, albeit with small SSA.
- Pore surface reactivity modified to increase heat of adsorption; SSA and pore volume unaffected.
- Applicable to CDC pore surfaces?

<table>
<thead>
<tr>
<th>Treatment</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>

Aminated nanodiamond surfaces show > 2X H₂ uptake relative to clean surfaces, over a wide range of H₂ pressure.
Metal doping: another route to enhanced H₂ binding

Calculations on Ti-decorated C60 reveal enhanced H₂ binding via d-orbital hybridization (Kubas) and suggest ethylene as surrogate for sp²-disordered carbons.

PRL 94, 175501 (2005)

Replacing Ti with Li affords C₂H₄(Li-2H₂)₂ with 16.0 wt% capacity.

PRB 76, 085434 (2007)

Ti-decorated ethylene binds 10 H₂ molecules w/o decomposing C₂H₄: 14 wt% capacity.

PRL 97, 226102 (2006)

Laser ablation of Ti in C₂H₄; deposit thin film on surface acoustic wave microbalance. H₂ exposure gives 14% wt. uptake; doubled with D₂.

PRL 100, 105505 (2008)
Alkali metal doping: TiC-CDC

**2007 – Li_{1.6}C_{100}**

Little or no effect at 1.6% level; higher concentration increases risk of blocking pores with Li clusters.

**2008 – sodium**

- **Na_{4.4}C_{100}**
  - Slight reduction compared to undoped: 3.0 vs. 3.8 wt% at 77K. Similar $\Delta H$; no evidence for NaH$_2$ at 300K.

- **Na_{6}C_{100}**
  - Significant reduction compared to undoped; roughly by half. $\Delta H$ also severely reduced.

**Challenges:** maintain uniform doping; avoid blocking pores with metal clusters.
Ti doping for Kubas “binding”

• First attempts (2007) involved exposing annealed CDC to TiCl₄, then heating and performing a second H₂ cleanup.
• Ti/C ratio in the range 1-2 at%; HRTEM shows Ti nanoclusters.
• Slight reduction in capacity at 77K and high pressure; significant increase in (very low) capacity at 300K and all pressures.
Plasma reaction of hydrocarbon + TiCl₄

H₂ flow rate controls the particle size

C₂H₂ for sp² vs. C₄H₄ for sp³

Microplasma can be tailored for thermal or non-thermal processes: thin film deposition, graphitic or polymeric particles, diamond-like or amorphous carbon.

Status: assembly and testing complete; first runs produced very small amounts. Currently optimizing plasma conditions.
Local structure of CDC’s
(North Carolina State University)

Process Diagram for Modeling and Characterizing Amorphous Carbons Using Atomistic Simulation Techniques

- Structure Factor $S(q)$
- Skeletal Density
- Coordination Constraint

Optimized spatial coordinates of ~2000 C atoms.

Next: compare isotherms and heats w/expt. Learn how pores evolve with processing; etc. Key to rational design/optimization of CDC’s.
Future work

• Fully optimize activation protocol for CDC and produce material with 1 cm³/g volume of pores of <1 nm and 1.5-2 cm³/g of pores <1.5 nm.
• Adjust plasma parameters to obtain ~100 mg quantities of Ti-doped CDC; verify atomic dispersion; determine if capacity is enhanced thereby.
• Apply surface treatments, especially amination, to CDC; measure effects on effective SSA, isosteric heat, capacity etc.
• With aid of database, identify candidates for sequential application of activation, surface treatment and/or doping.
• Exploit HRMC coordinates to calculate isosteric heats, isotherms etc. to help correlate pore structure and performance.
• Key milestone: gravimetric excess (material) capacity at the level of the best MOFs.
• Project ends 9/08; anticipate 6 month no-cost extension to 3/09.
Summary

- Purified CDC’s subjected to chemical or physical activation can match, or slightly exceed, gravimetric capacity of activated carbons. The key is careful control of pore size and size distribution, while maximizing SSA.

- Large pores (d > 1.5 nm) are less effective than small ones, both at high and low pressure. Increasing SSA by activation is only useful if the volume of small pores, preferably below 1 nm, is thereby increased.

- Results on TiC-CDC at low T and high P need to be extended to other CDC families, in search of high performance at lower T and P.

- This may be achieved by increasing isosteric heat of adsorption via surface treatment or light transition metal doping.

- New partner Y-Carbon licensed to develop the technology, in particular scale-up the manufacturing of CDC. Y-Carbon has received $243,835 in funding from Pennsylvania NanoMaterials Commercialization Center (www.pananocenter.org).