Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

John E. Fischer[1,3], Yury Gogotsi[2] 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-13

Overview

Timeline

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

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

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

➢ 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 H_2 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).

purify/anneal in H_2 or NH_3

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.

"ACTIVATION"
Increases SSA and total pore volume in many carbons. We know that pores < 1 nm dominate H_2 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. H_2 Sieverts and SSA measurements after exposure to gases.
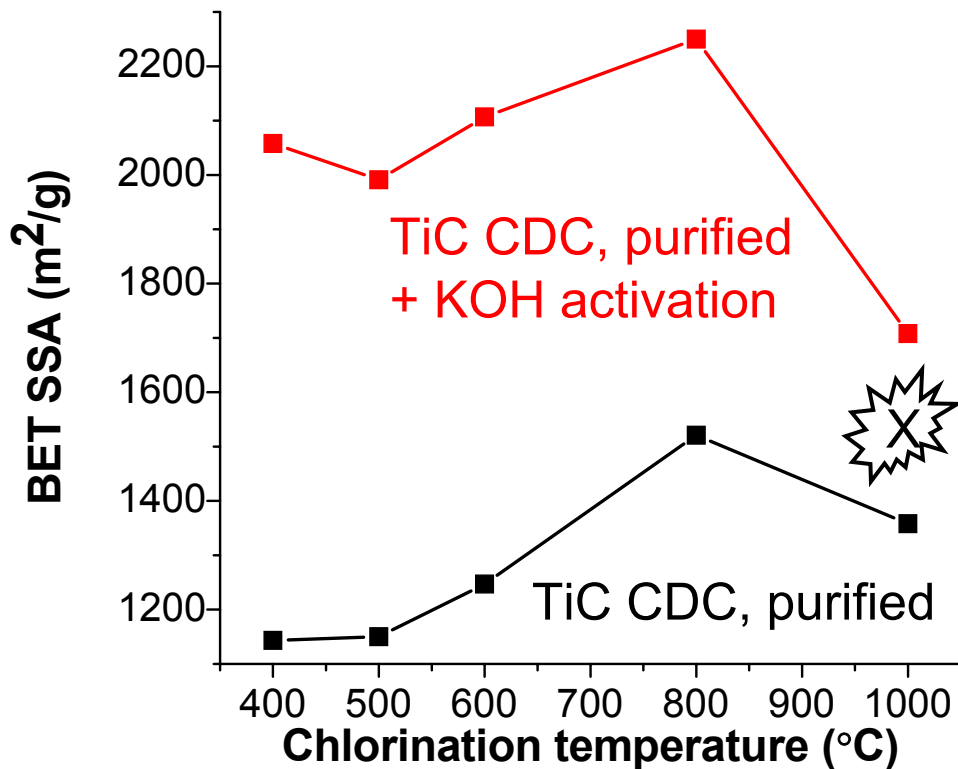
DOPING (Li, K, Ti, Ni)
Develop atom-scale metal center interactions (**not** catalysis) to enhance H_2 binding with carbon network - e.g. Dewar/Kubas d-orbital hybridization – avoid forming nanoclusters, blocking pores.

Characterization: Raman, TEM, EDS, WAXS and PGAA for purity and state of the carbon network;
Performance: sorption with various gases (SSA, PSD's etc), H_2 isotherms 30-300K and 1-50 atm.; SAXS

Chemical activation with KOH (Alicante)

TiC CDC, purified + KOH activation

TiC CDC, purified

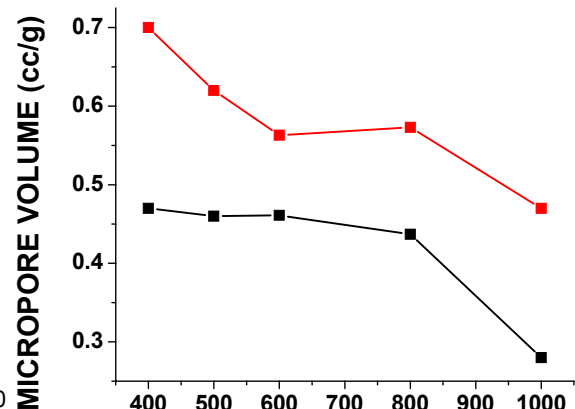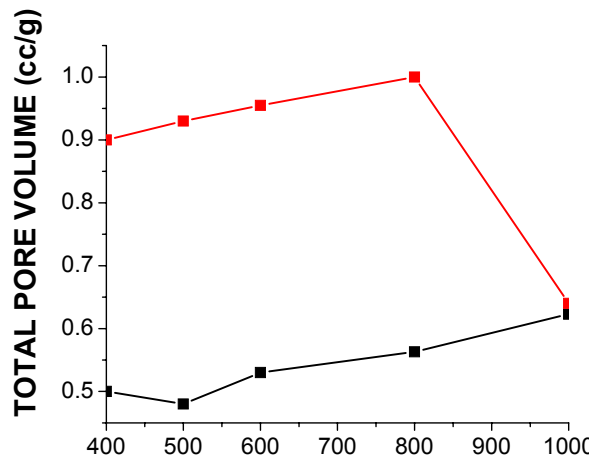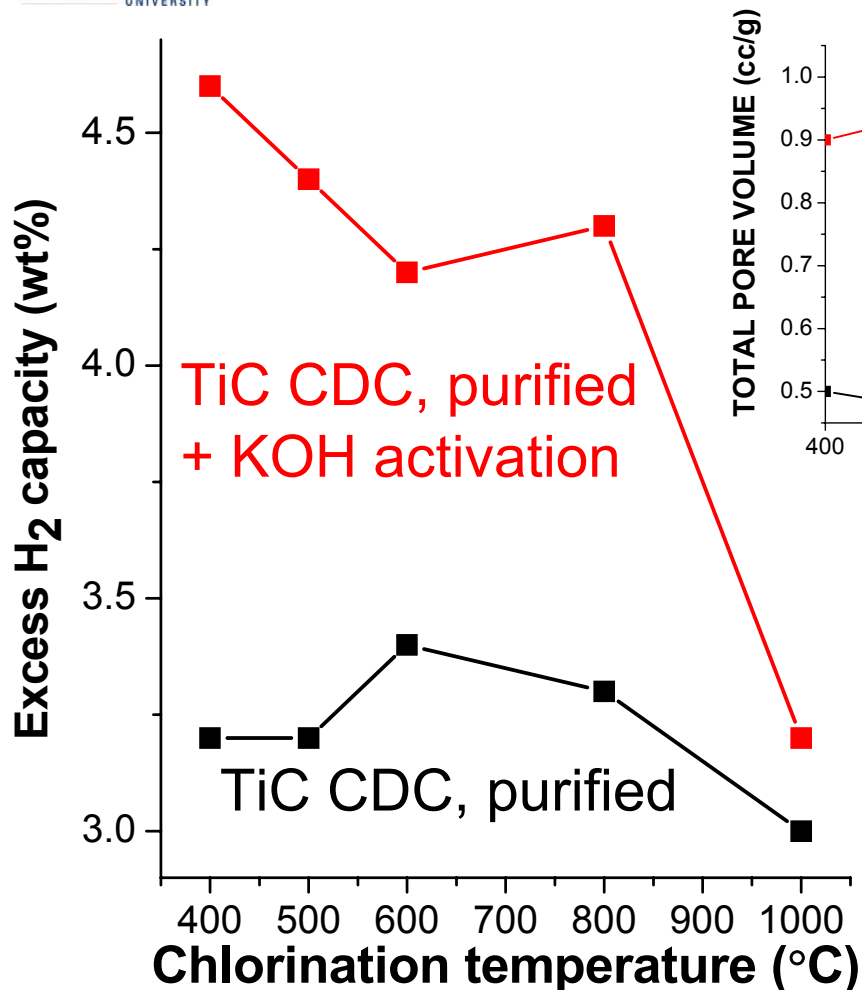BET SSA (m^2/g) vs Chlorination temperature (°C)

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.

# Pore volume, micropore volume and excess gravimetric capacity (77K, 60 bar)

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 @ 600C
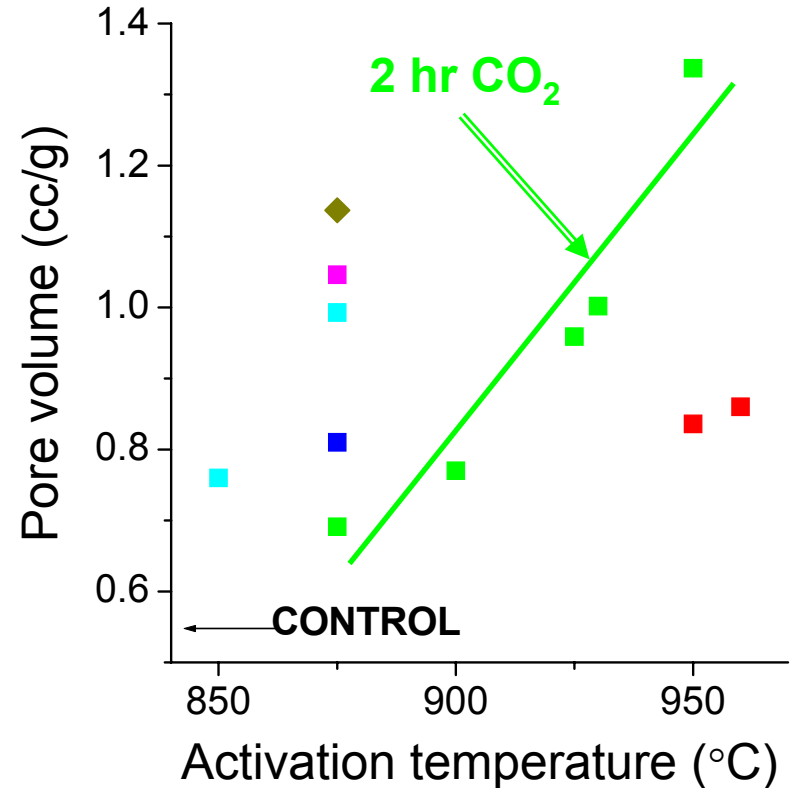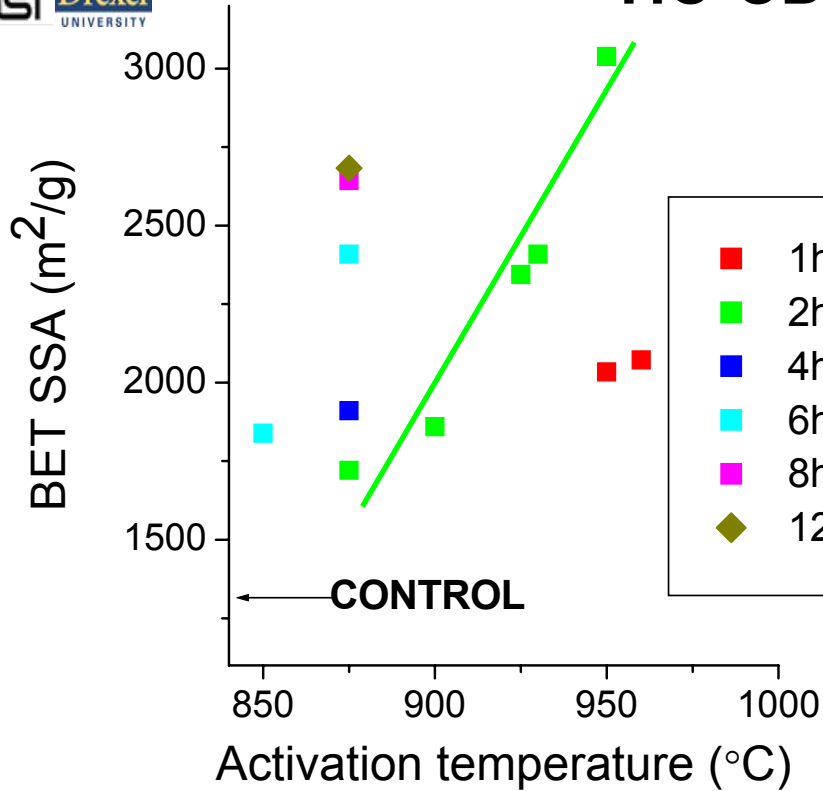
- CO_2 is a milder oxidant than air but higher burn-off (lower yield) than KOH.
- 50% yield at 875°C; decreases notably at higher CO_2 temperatures.
- 8 hrs required to saturate the process at 875 °C.
- At fixed 2 hr time, SSA and pore volume increase linearly with increasing $T(CO_2)$.

CO_2 increases SSA and pore volume by up to 130%.

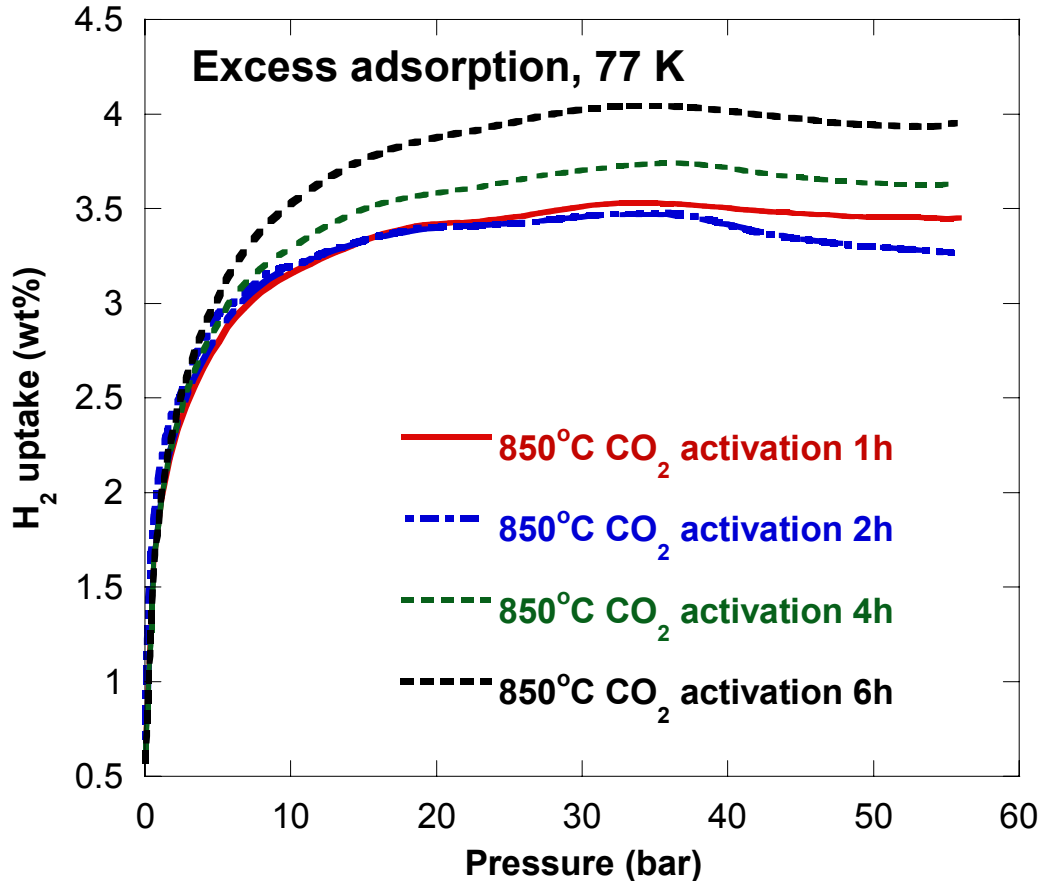# Effect on H₂ storage: a tradeoff between SSA and micropore volume

CO₂-activated TiC@600C
60 bars, 77K

0°C isotherm w/CO₂
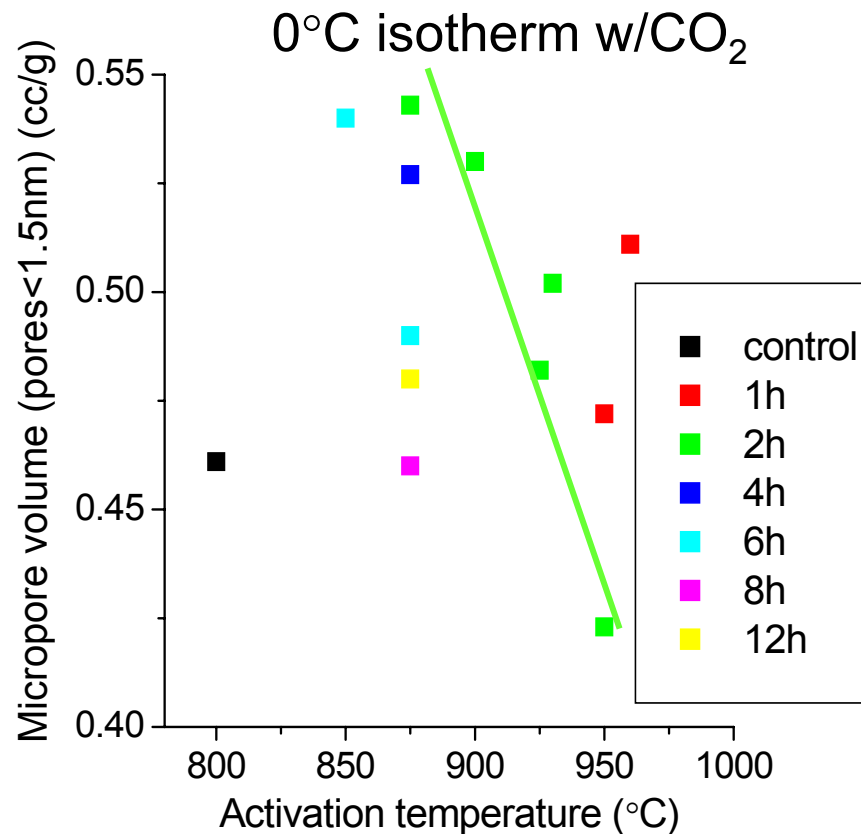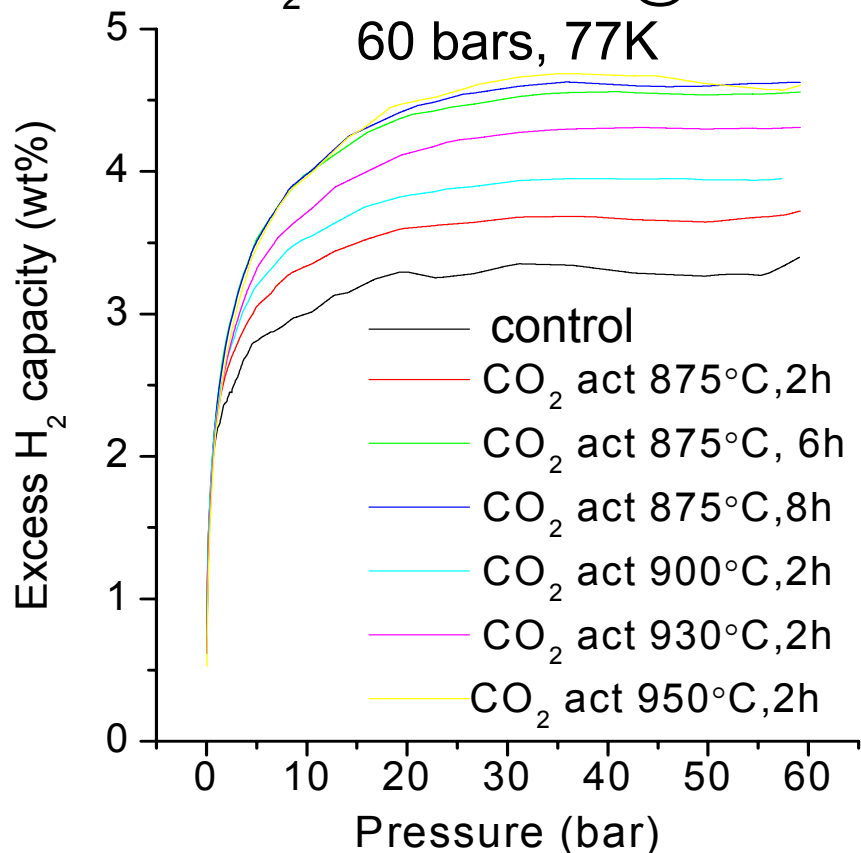
Up to 50% enhancement of gravimetric capacity, either with SSA > 3000 and some large pores (950C, 2 hr.), or SSA = 2700 and no large pores (875C, 8 hr.)

H_2 storage in CO_2 - activated SiC-CDC

Excess adsorption, 77 K

H_2 uptake (wt%) vs Pressure (bar)

- —— 850°C CO_2 activation 1h
- –·–· 850°C CO_2 activation 2h
- ---- 850°C CO_2 activation 4h
- ---- 850°C CO_2 activation 6h

Without activation, purified SiC-CDC underperform their TiC counterparts because the volume of pores < 1 nm. is smaller. Optimized CO_2 activation brings SiC-CDC performance into the range of activated TiC-CDC.
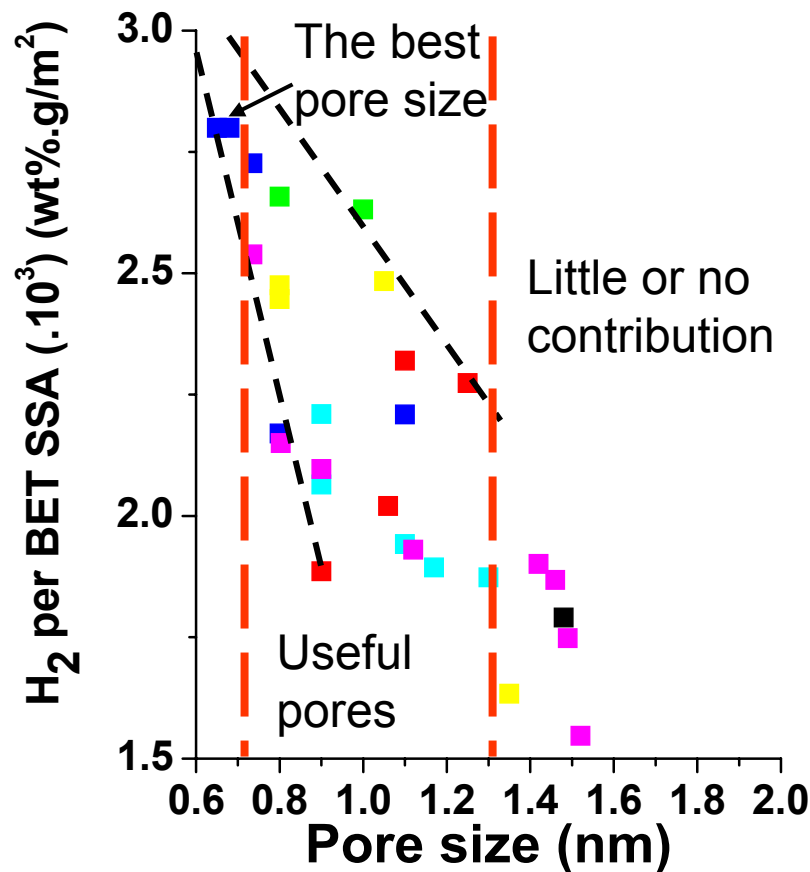

- SiC 1100C
- after CO2 @ 900C, 25 ccm, 2 hr.

pore volume (cc/g) vs pore width (nm)
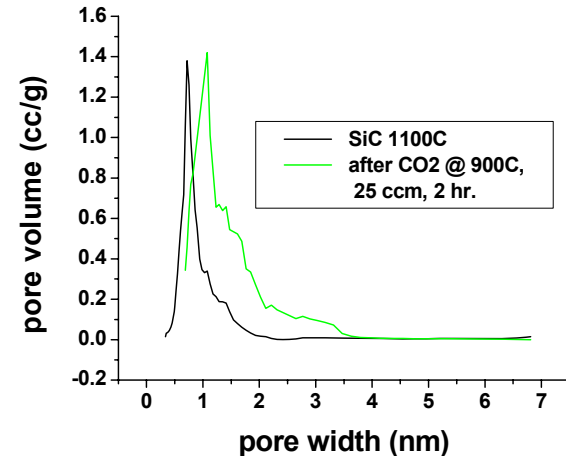
Any CDC which shows increased micropore volume after activation will show significantly enhanced H_2 capacity.

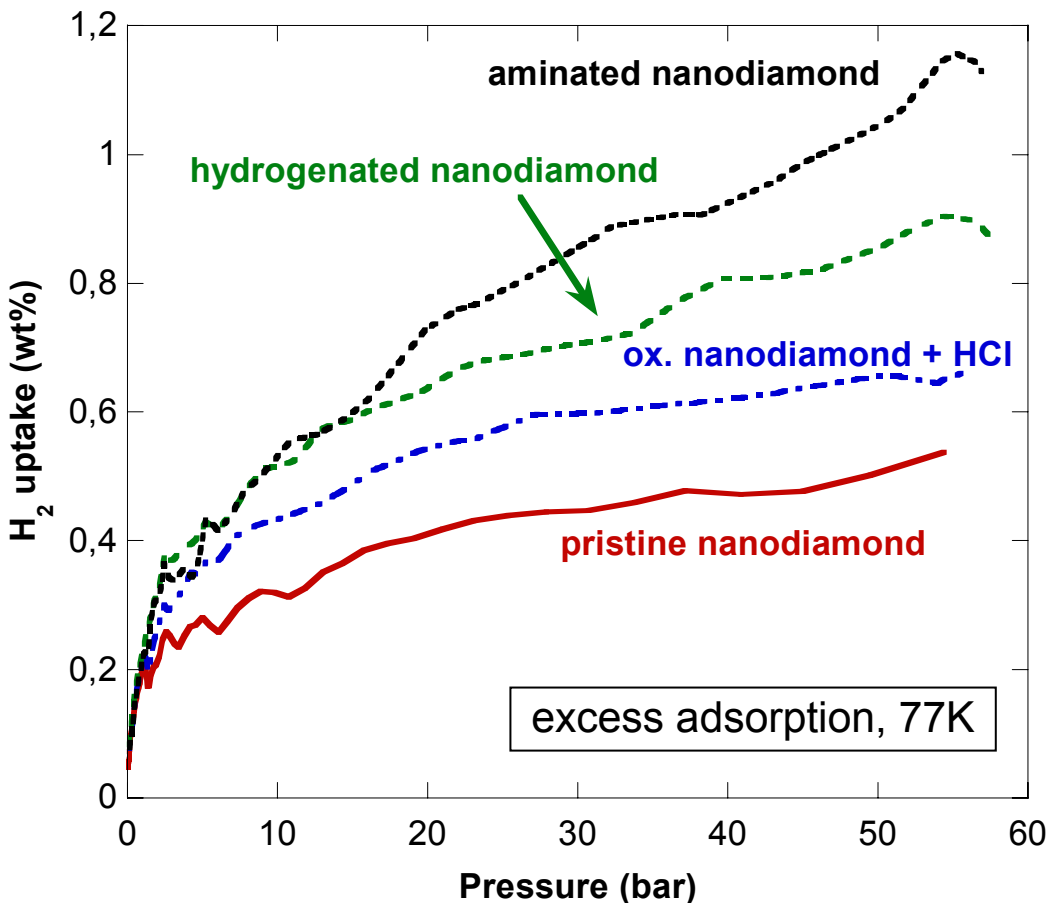# Correlation of 60 bar 77K storage with SSA and volume of small pores
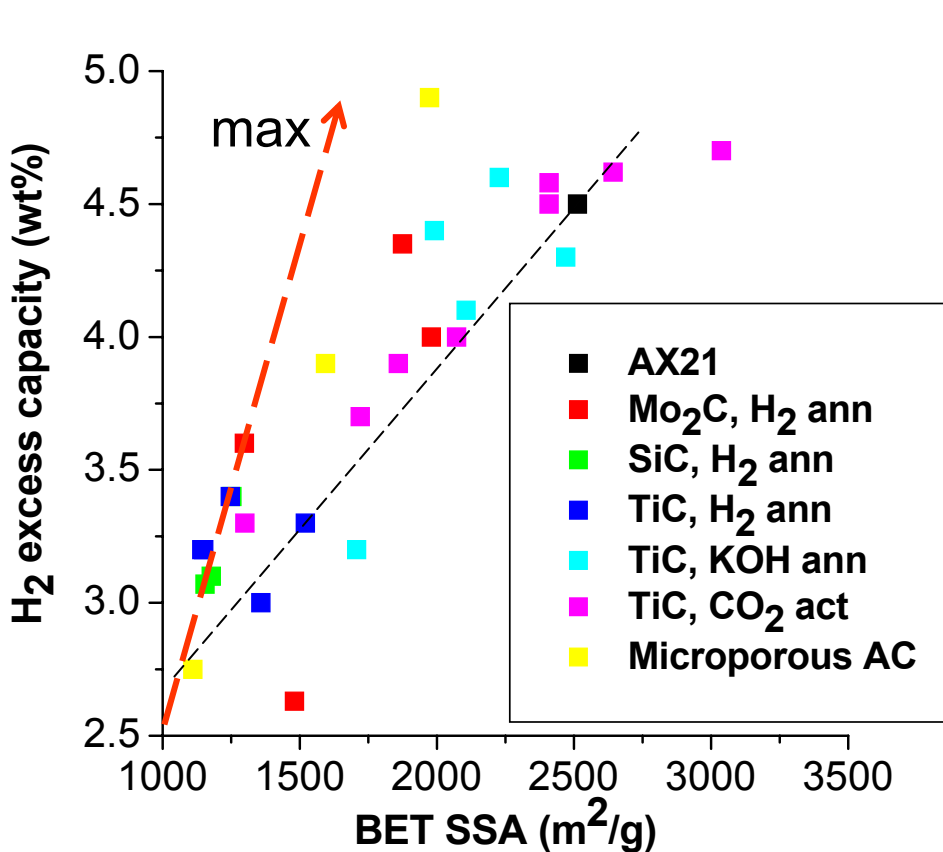
Overall, linear dependence of storage on BET SSA, similar to 1 atm.

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

aminated nanodiamond

hydrogenated nanodiamond

ox. nanodiamond + HCl

pristine nanodiamond

excess adsorption, 77K

H₂ uptake (wt%) — y-axis: 1,2 / 1 / 0,8 / 0,6 / 0,4 / 0,2 / 0

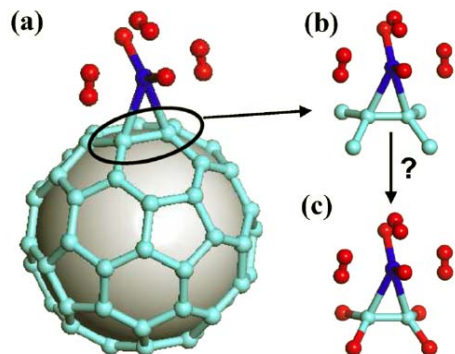**Pressure (bar)** — x-axis: 0 / 10 / 20 / 30 / 40 / 50 / 60

- 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?

Treatment	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

Aminated nanodiamond surfaces show > 2X H_2 uptake relative to clean surfaces, over a wide range of H_2 pressure.

Metal doping: another route to enhanced H$_2$ binding

$C_2H_4(Ti-5H_2)_2$

(d)

Ti-decorated ethylene binds 10 H$_2$ molecules w/o decomposing C$_2$H$_4$: 14 wt% capacity.
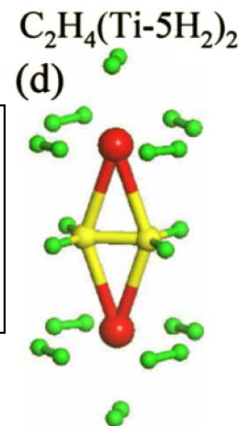PRL **97**, 226102 (2006)

Calculations on Ti-decorated C60 reveal enhanced H2 binding via d-orbital hybridization (Kubas) and suggest ethylene as surrogate for sp2-disordered carbons.
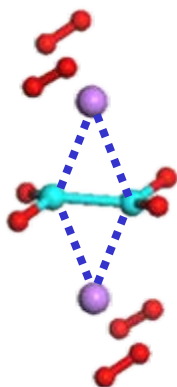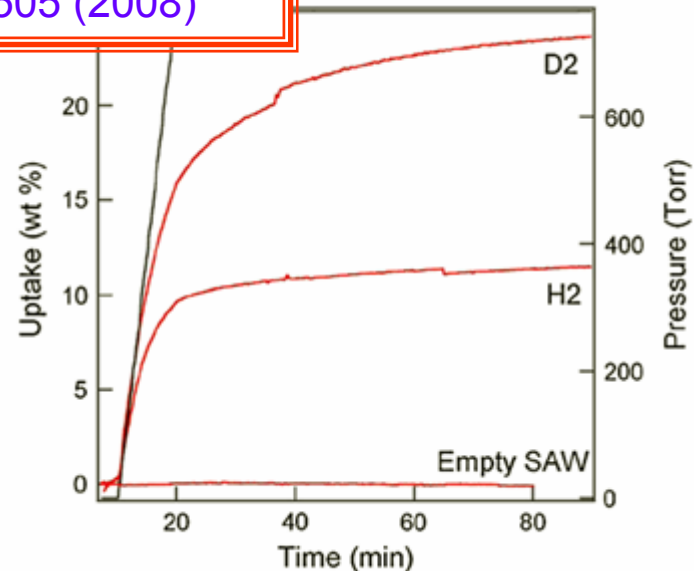PRL **94**, 175501 (2005)

Laser ablation of Ti in C$_2$H$_4$; deposit thin film on surface acoustic wave microbalance. H$_2$ exposure gives 14% wt. uptake; doubled with D$_2$.
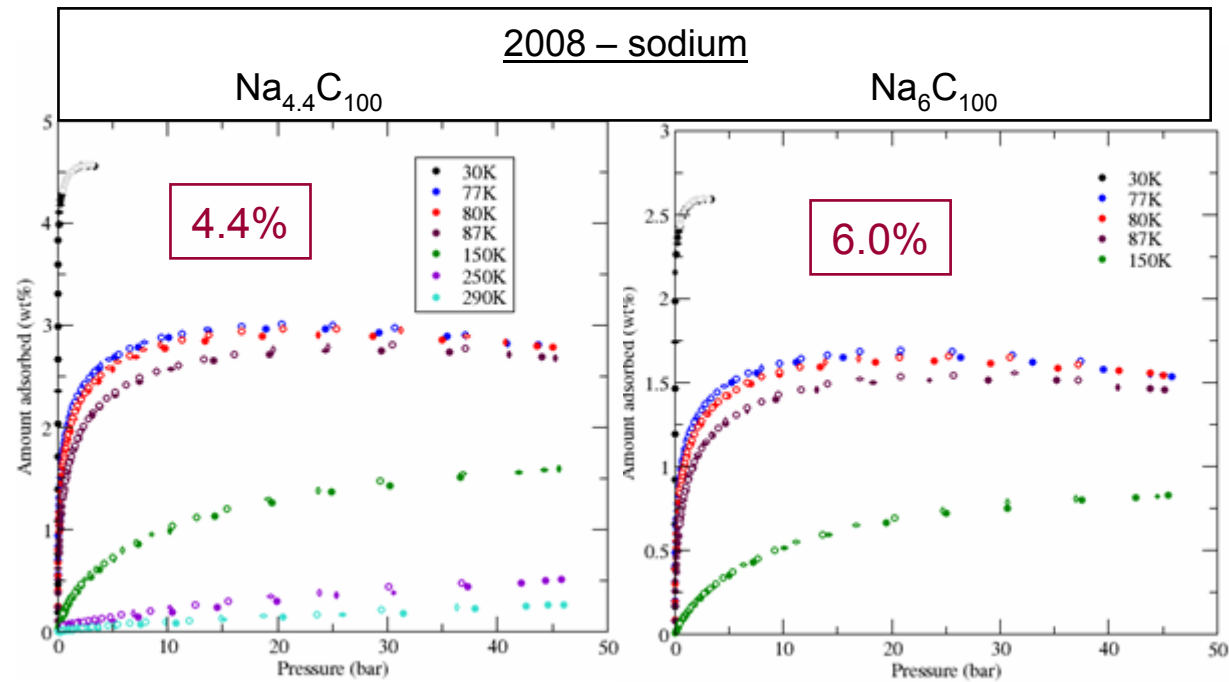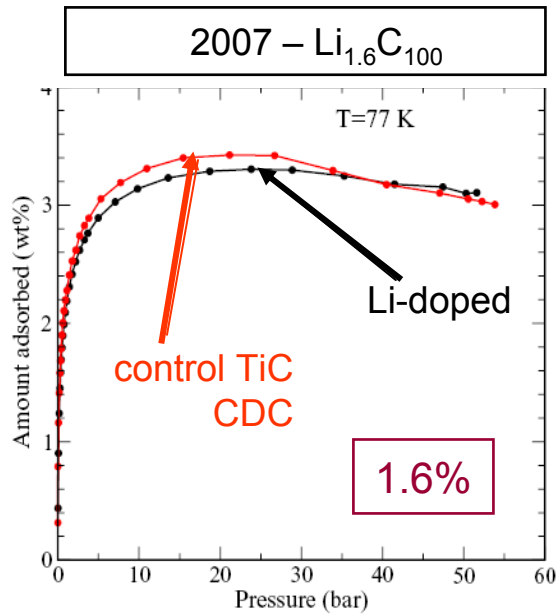PRL **100**, 105505 (2008)

Replacing Ti with Li affords C$_2$H$_4$(Li-2H$_2$)$_2$ with 16.0 wt% capacity.
PRB **76**, 085434 (2007)

(a) (b) (c) ?

Alkali metal doping: TiC-CDC

2007 – Li$_{1.6}$C$_{100}$

T=77 K

Li-doped

control TiC CDC

1.6%

2008 – sodium

Na$_{4.4}$C$_{100}$

4.4%

30K
77K
80K
87K
150K
250K
290K

Na$_6$C$_{100}$

6.0%

30K
77K
80K
87K
150K

Little or no effect at 1.6% level; higher concentration Increases risk of blocking pores with Li clusters.
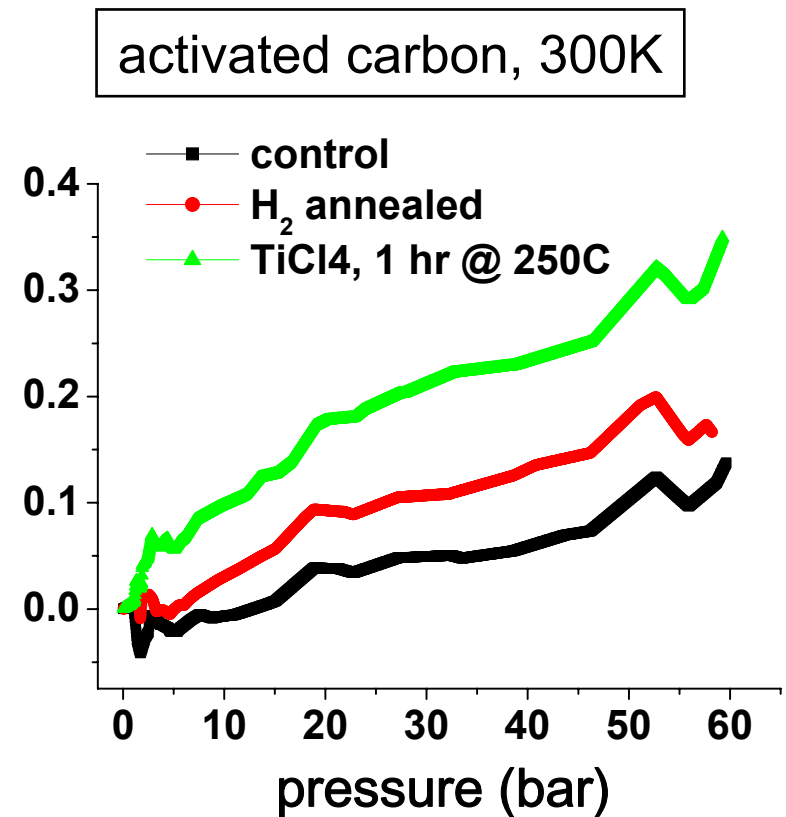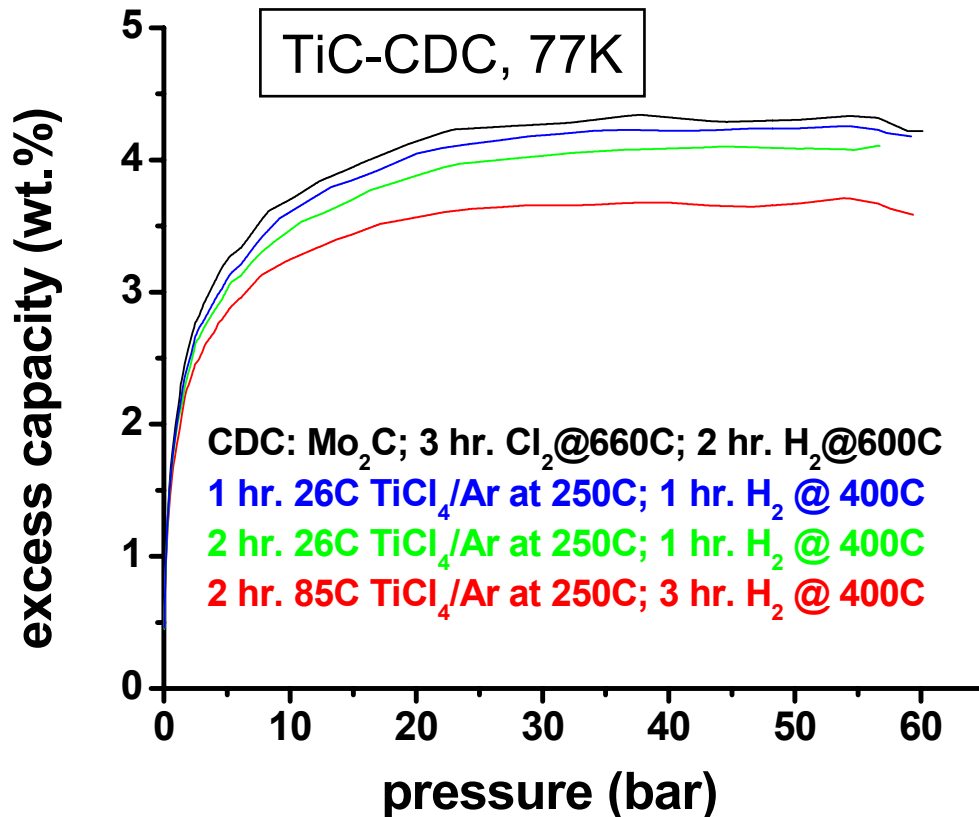
Slight reduction compared to undoped: 3.0 vs. 3.8 wt% at 77K. Similar ΔH; no evidence for NaH$_2$ at 300K.

Significant reduction compared to undoped; roughly by half. ΔH also severely reduced.

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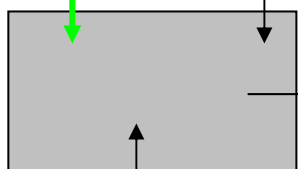
Ti doping for Kubas "binding"

- First attempts (2007) involved exposing annealed CDC to $TiCl_4$, then heating and performing a second H_2 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.

TiC-CDC, 77K

activated carbon, 300K

CDC: Mo_2C; 3 hr. Cl_2@660C; 2 hr. H_2@600C
1 hr. 26C $TiCl_4$/Ar at 250C; 1 hr. H_2 @ 400C
2 hr. 26C $TiCl_4$/Ar at 250C; 1 hr. H_2 @ 400C
2 hr. 85C $TiCl_4$/Ar at 250C; 3 hr. H_2 @ 400C

- control
- H_2 annealed
- TiCl4, 1 hr @ 250C

excess capacity (wt.%)

pressure (bar)

pressure (bar)

Plasma reaction of hydrocarbon + TiCl$_4$

H$_2$ flow rate controls the particle size

C$_2$H$_2$ for sp^2
vs. C$_4$H$_4$ for sp^3

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

exhaust

Gas flow

TiCl$_4$ bubbler

particle collection system.
Target: 100 mg with 5-10% Ti

water bubbler to capture Cl

buffer (N$_2$, Ar, He) 10-1000 sccm also controls particle size
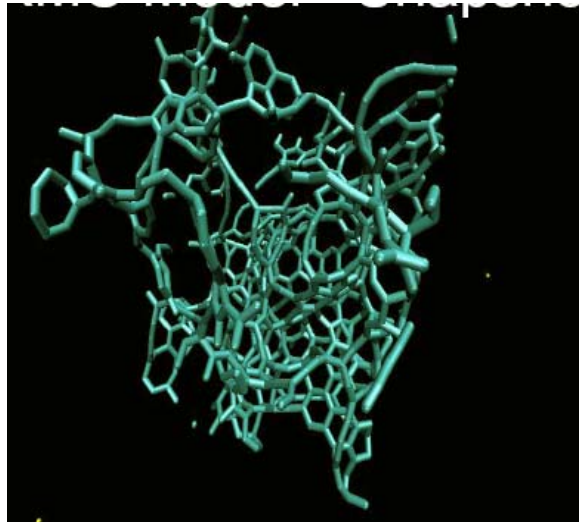
Status: assembly and testing complete; first runs produced very small amounts. Currently optimizing plasma conditions.

Local structure of CDC's
(North Carolina State University)

neutron scattering
$0.1 < Q < 40\ A^{-1}$
(IPNS, now LANL)

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

- Structure Factor S(q)
- Skeletal Density
- Coord. Constraint

MCGR

Pair Correlation Function g(r)

HRMC
- Skeletal Density
- Composition
- Reactive Potential

STRUCTURAL ANALYSIS
- Ring Statistics
- Ring Connectivity
- Bond Angle Dist
- Bond Length Dist
- Pore Size Dist
- Zero Coverage q_{st}
- "TEM" Images

Model Structure

Optimized spatial coordinates of ~2000 C atoms.

GCMC
- Adsorption Isotherms
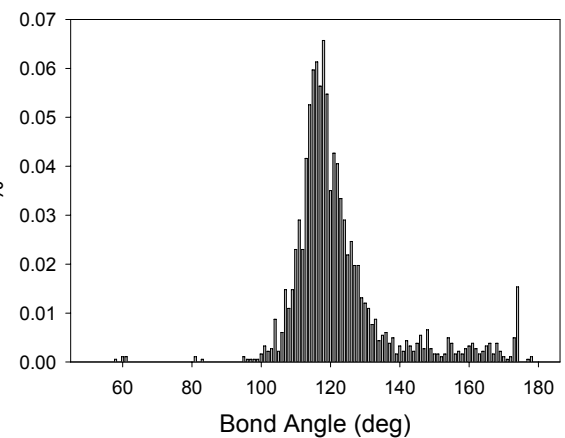- Isosteric Heats

- Equilibrium Configurations

MD
- Diffusivities

HRMC: Hybrid Reverse Monte Carlo **GCMC**: Grand Canonical Monte Carlo **MD**: Molecular Dynamics

Bond Angle Distribution CDC-800K

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 cm^3/g volume of pores of <1 nm** and

  1.5-2 cm^3/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; mesaure 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).