Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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Abstract

Carbide derived carbons (CDCs) represent a new class of nanoporous carbons produced by selective thermo-chemical etching of metal atoms from carbides. CDCs have BET specific surface area of up to 2000 m^2/g and up to 80% open pore volume available for hydrogen storage. The structure and porosity of CDC can be controlled by the structure of the carbide precursor as well as the process parameters, including synthesis temperature and environment. These properties, combined with a low cost, make CDC a potential candidate for hydrogen storage. In this work, CDCs produced from B_4C, ZrC, TiC, and SiC were evaluated for their hydrogen storage capacity. Hydrogen sorption measurements were performed at 77K by a volumetric method using a Quantachrome Autosorb-1 gas sorption analyzer. The amount of hydrogen adsorbed at atmospheric pressure reached 3 wt.%.

Overview

Timeline

- Project start: 10/1/2004
- Project end: 2008
- Percent completed: ~15%

Budget

- Total project funding (expected) $1,377,000
  - DOE share 80%
  - Contractor share 20%
- Funding for FY05: $300,000

Barriers

- Need a better control over pore structure and microstructure of CDCs.
- Low throughput of hydrogen storage measurements (need additional gas sorption equipment).

Partners

- Collaboration with various companies if planned

Distribution of Work

Drexel University

- Material synthesis
- Structural characterizations (Raman spectroscopy, X-ray diffraction)
- Porosity analysis using gas sorption technique
- Ambient pressure (1 atm) hydrogen storage measurements

University of Pennsylvania

- Small angle X-ray scattering (SAXS)
- Transmission electron microscopy (TEM)
- Activation

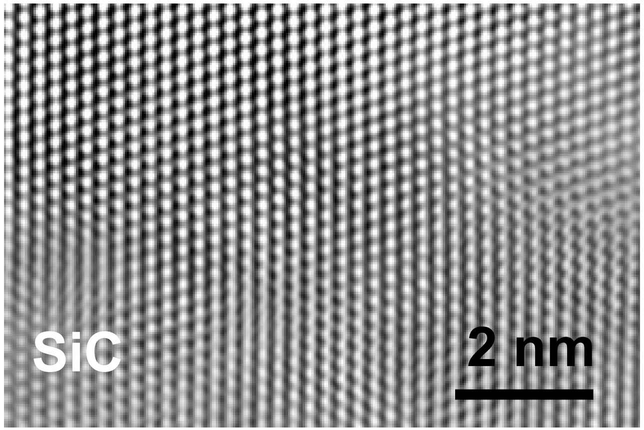
NIST

- High pressure hydrogen storage measurements
- Neutron scattering studies
- Simulation using density functional tight binding (DFTB) method

Carbide Derived Carbon (CDC)

$M_aC_{b(s)} + (c/2)Cl_{2(g)} \rightarrow aMCl_{c(g)} + bC_{(s)}$, where M represents metal

Carbide

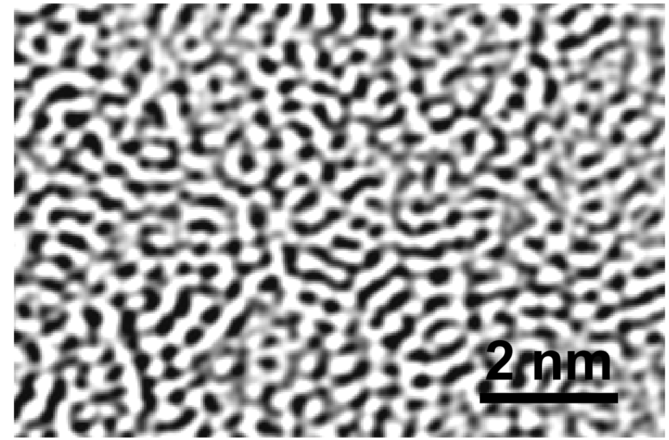


Etching Agent:
Cl_2, F_2, Br_2, I_2,
HCl, HBr, HI

$V_{SiC} = V_{CDC}$

Temperature:
200-1200°C

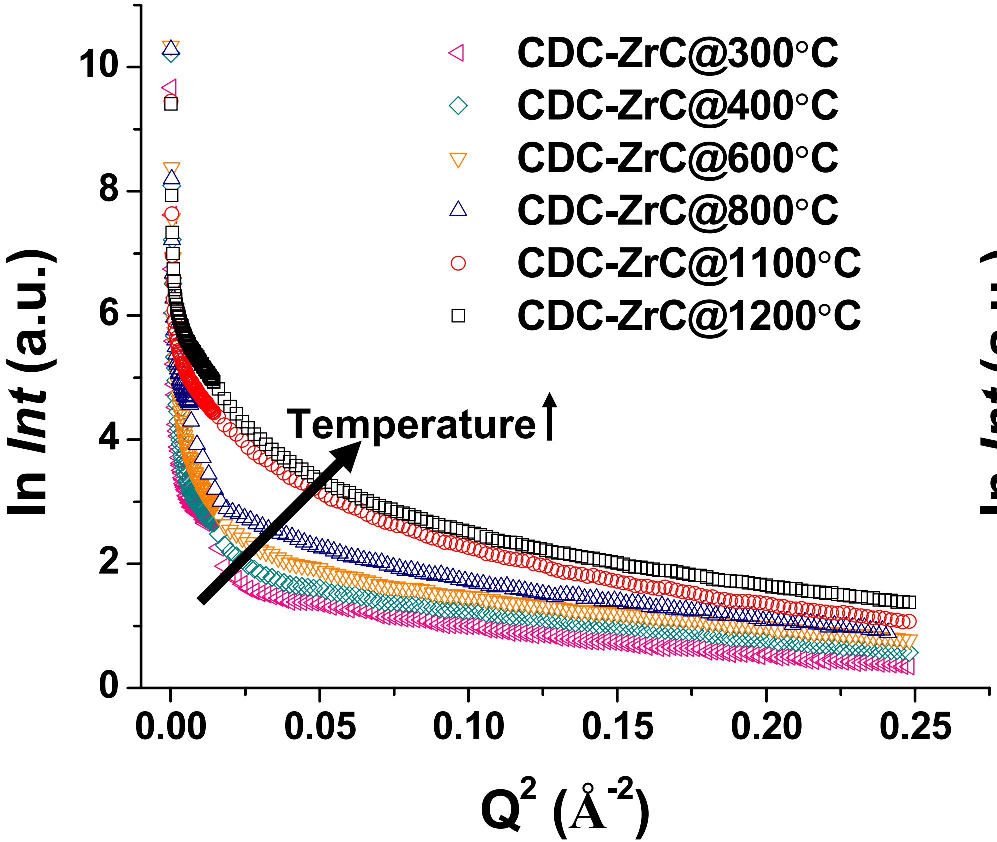
Carbide Derived Carbon

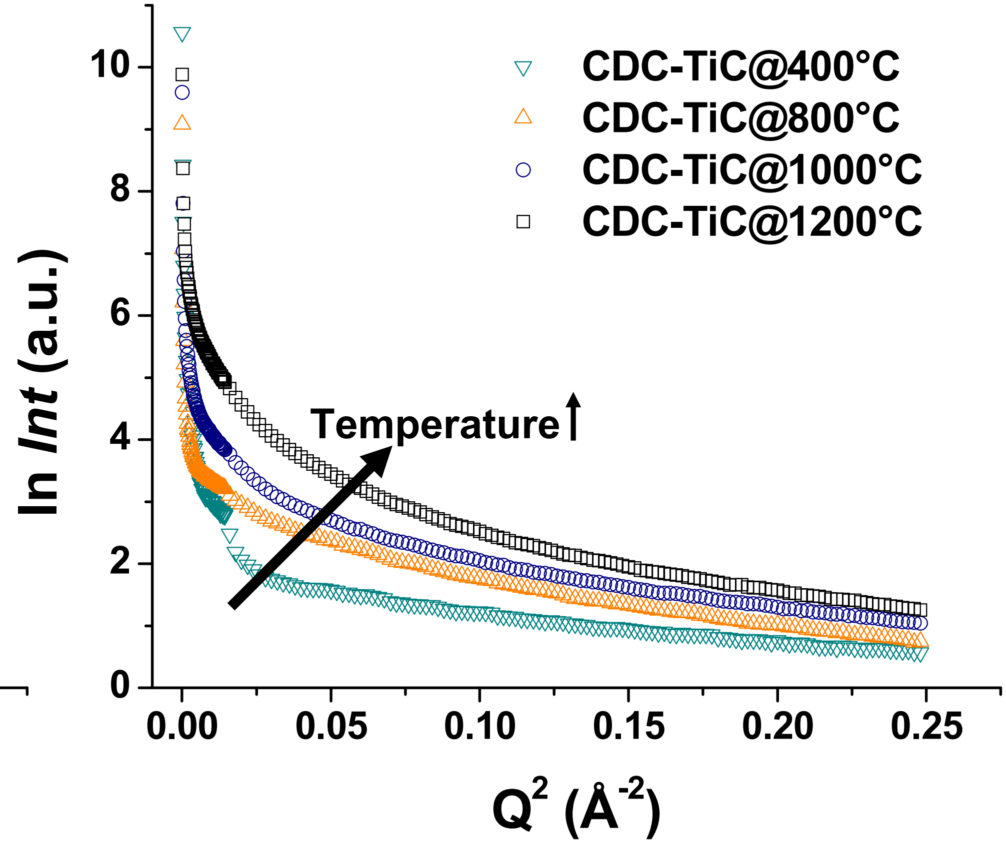


Process Features:

- Precise control over structure and pore size distribution in CDC
- Network of open pores
- Conformal (no size and shape change during transformation)
- Any metal carbide can be used
- Linear kinetics (can be grown to any thickness)
- Various forms: coatings, free standing monoliths and powder

SAXS Study

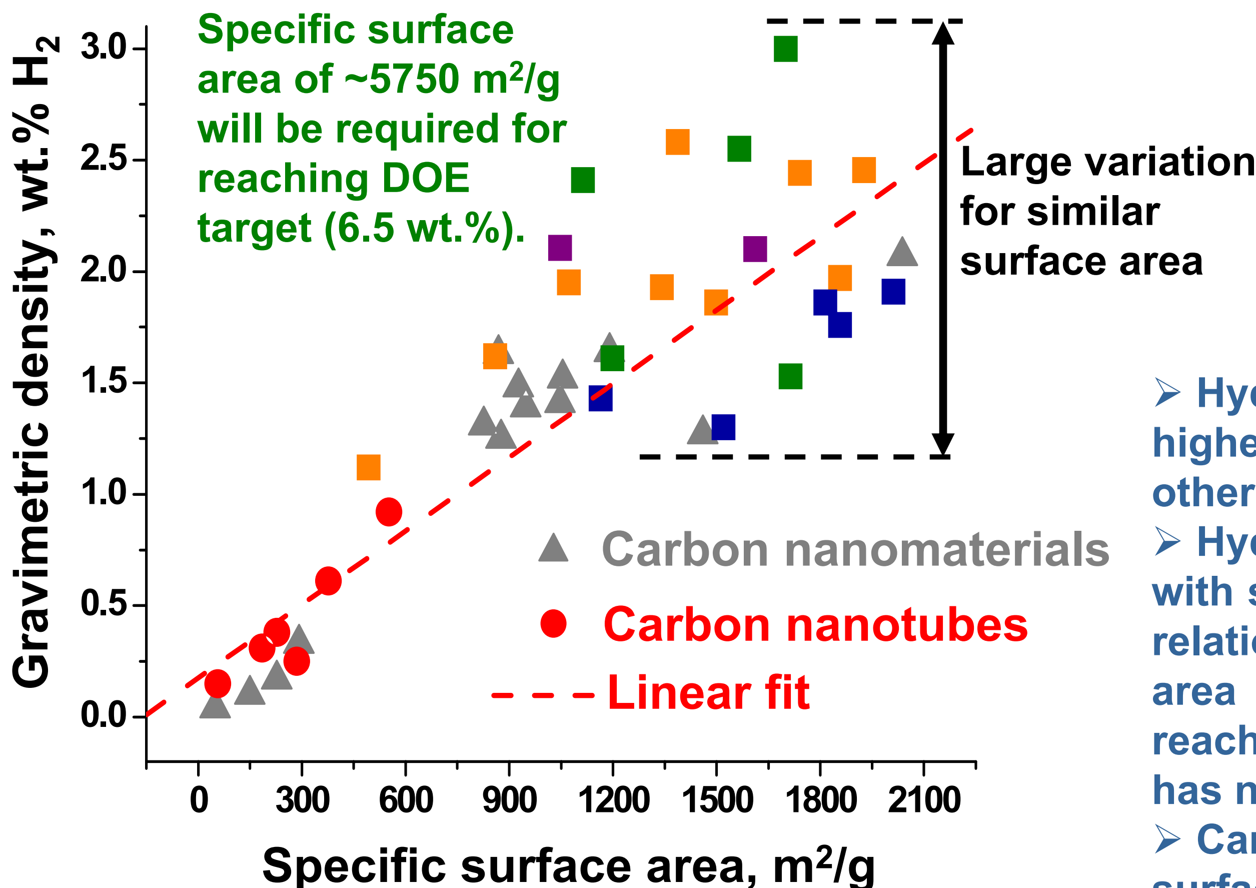


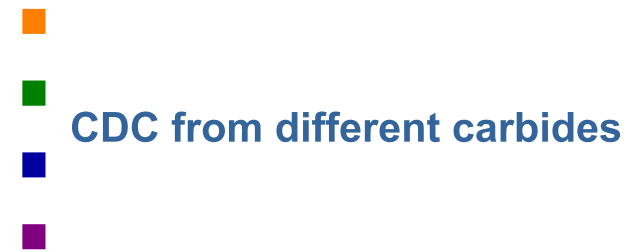


Small-angle X-ray scattering (SAXS) were performed on a multi angle diffractometer equipped with a Cu rotating anode, double focusing optics, evacuated flight path and a two-dimensional wire detector.

➢ Structure evolution with increasing processing temperature is confirmed by SAXS measurements

Effect of Surface Area on Hydrogen Storage

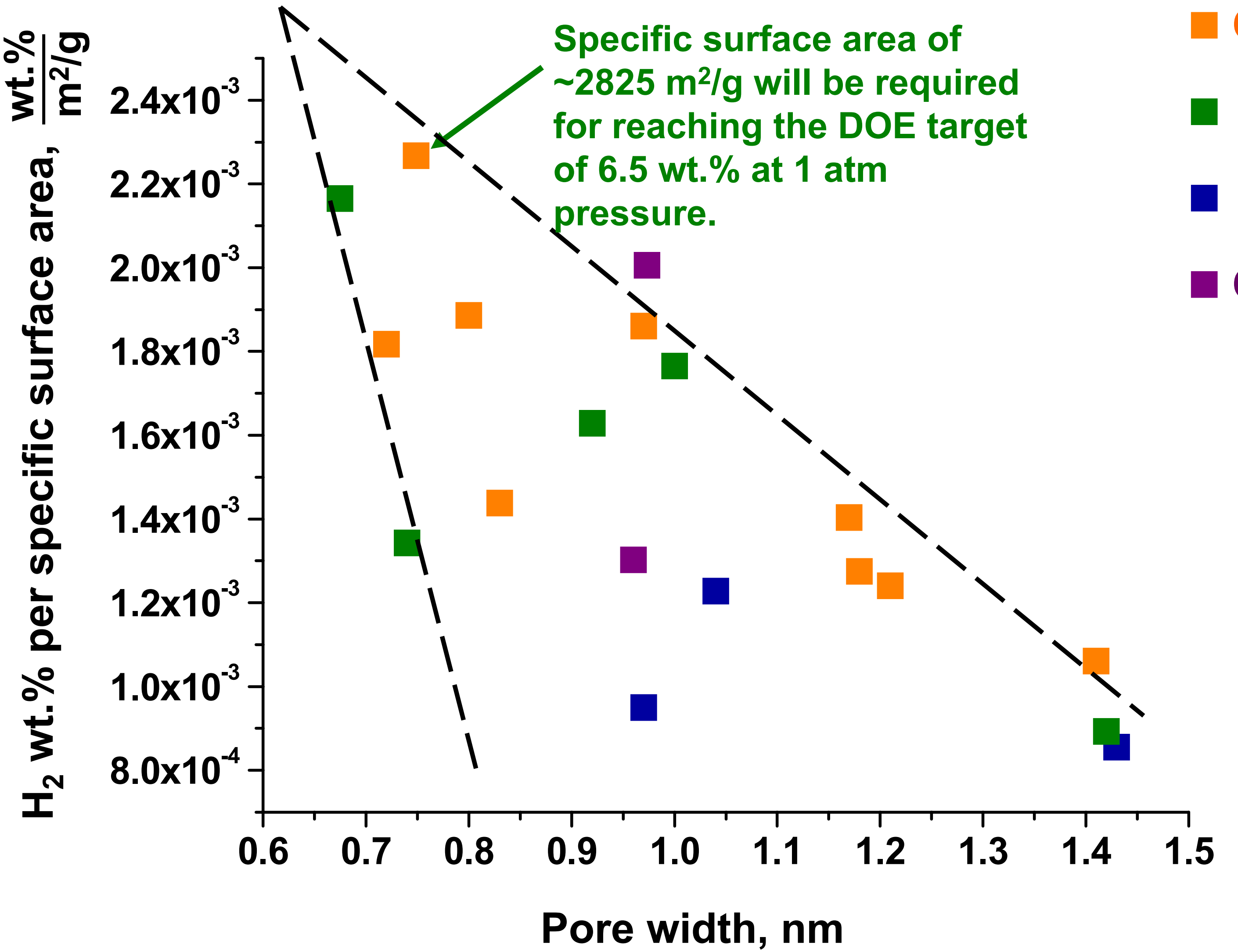




- ➢ Hydrogen storage capacity of CDCs is higher than that of carbon nanotubes and other carbon nanomaterials.
- ➢ Hydrogen storage capacity increases with surface area and extrapolation of this relationship shows that a specific surface area of ~5750 m^2/g will be required for reaching the DOE target, which to date has not been achieved.
- ➢ Carbon nanomaterials having similar surface area showed large variations in hydrogen storage capacity.
- ➢Analysis of the pore size/volume shows that the traditionally way of plotting hydrogen wt.% vs SSA is misleading.

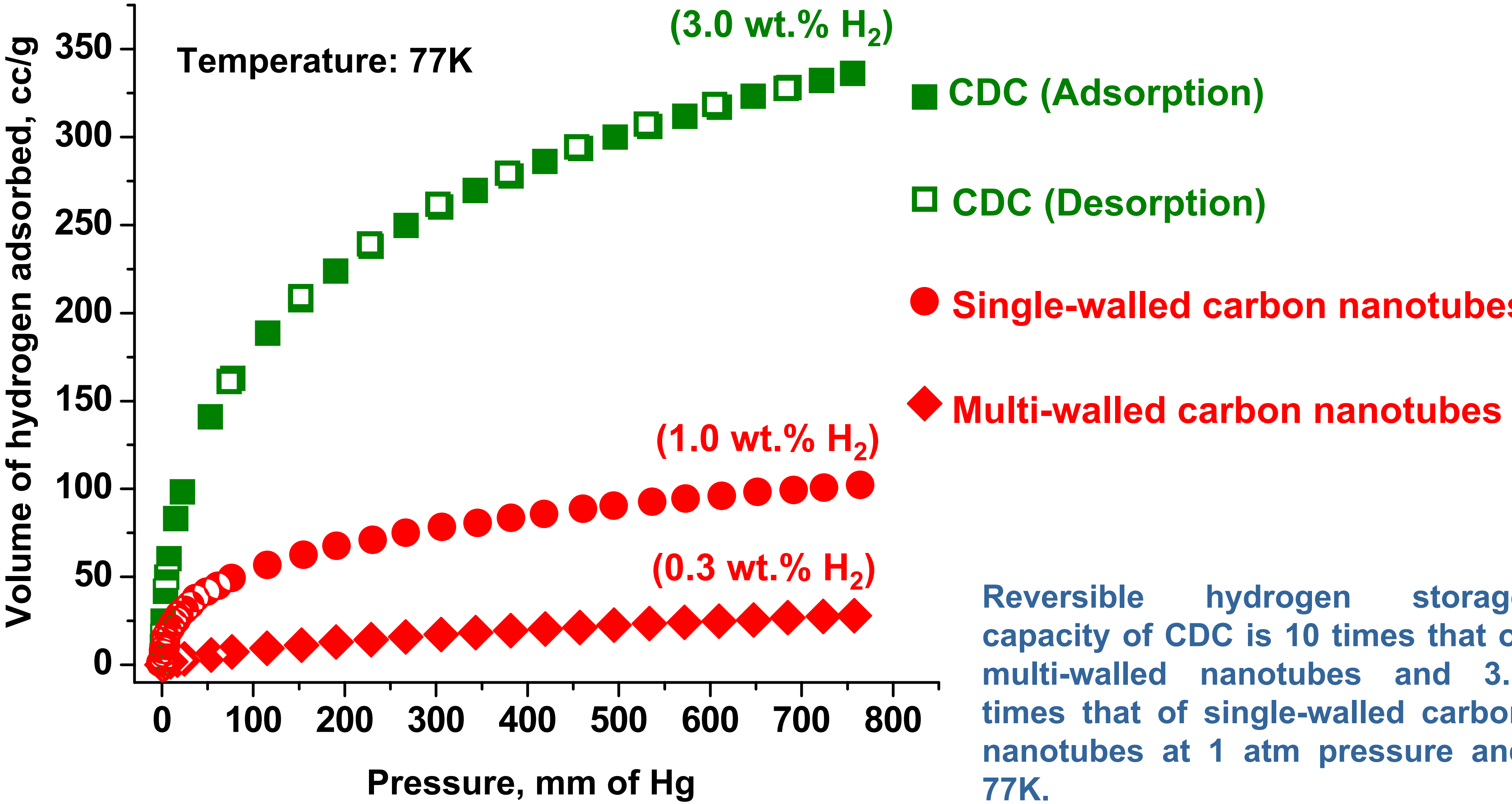
Hydrogen sorption measurements were performed using Quantachrome Autosorb-1 at 77 K and 1 atm pressure. Specific surface area was calculated according to BET (Brunauer, Emmet, Teller) equation for argon sorption at 77K.

Hydrogen Uptake per Surface Area vs. Pore Width in CDCs



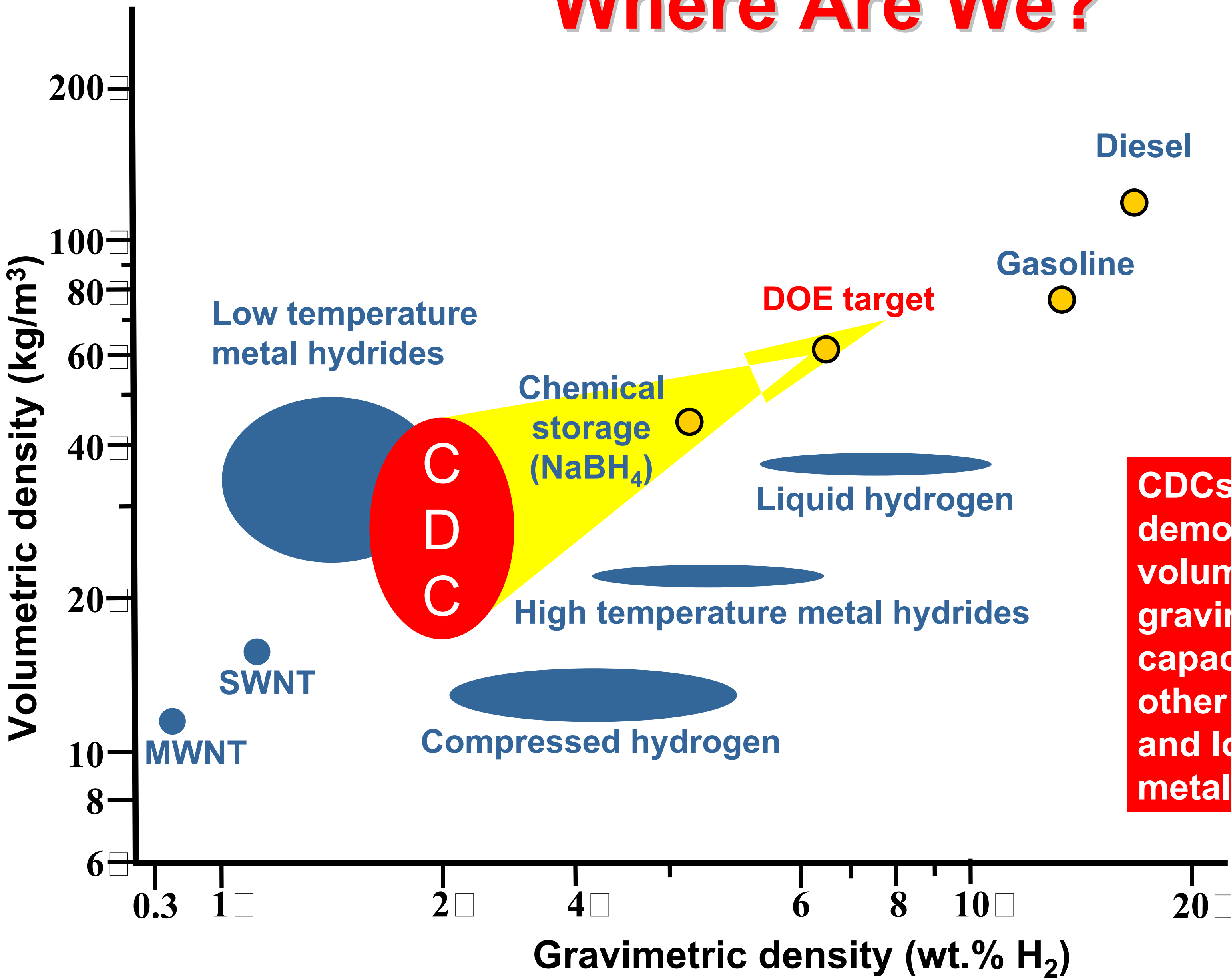
- Plotting hydrogen wt.% per specific surface area shows that the contribution of specific surface area to hydrogen storage capacity decreases with increase in pore width.
- Pores between 0.6 and 0.8 nm showed the highest hydrogen storage capacity per unit surface area.

Carbide Derived Carbon vs. Carbon Nanotubes



Reversible hydrogen storage capacity of CDC is 10 times that of multi-walled nanotubes and 3.5 times that of single-walled carbon nanotubes at 1 atm pressure and 77K.

Where Are We?



CDCs have already demonstrated a higher volumetric and gravimetric storage capacity compared to other carbon materials and low temperature metal hydrides.

Conclusions

- CDC is a nanoporous material with tunable pore size, specific surface area up to 2000 m^2/g and pore volume up to 1 cc/g available for hydrogen storage.

- At 1 atm pressure and 77K, CDCs has a gravimetric hydrogen storage density up to **3.0 wt.%** and volumetric density up to **40 kg/m^3**.

- Small pores arte more efficient for hydrogen storage.

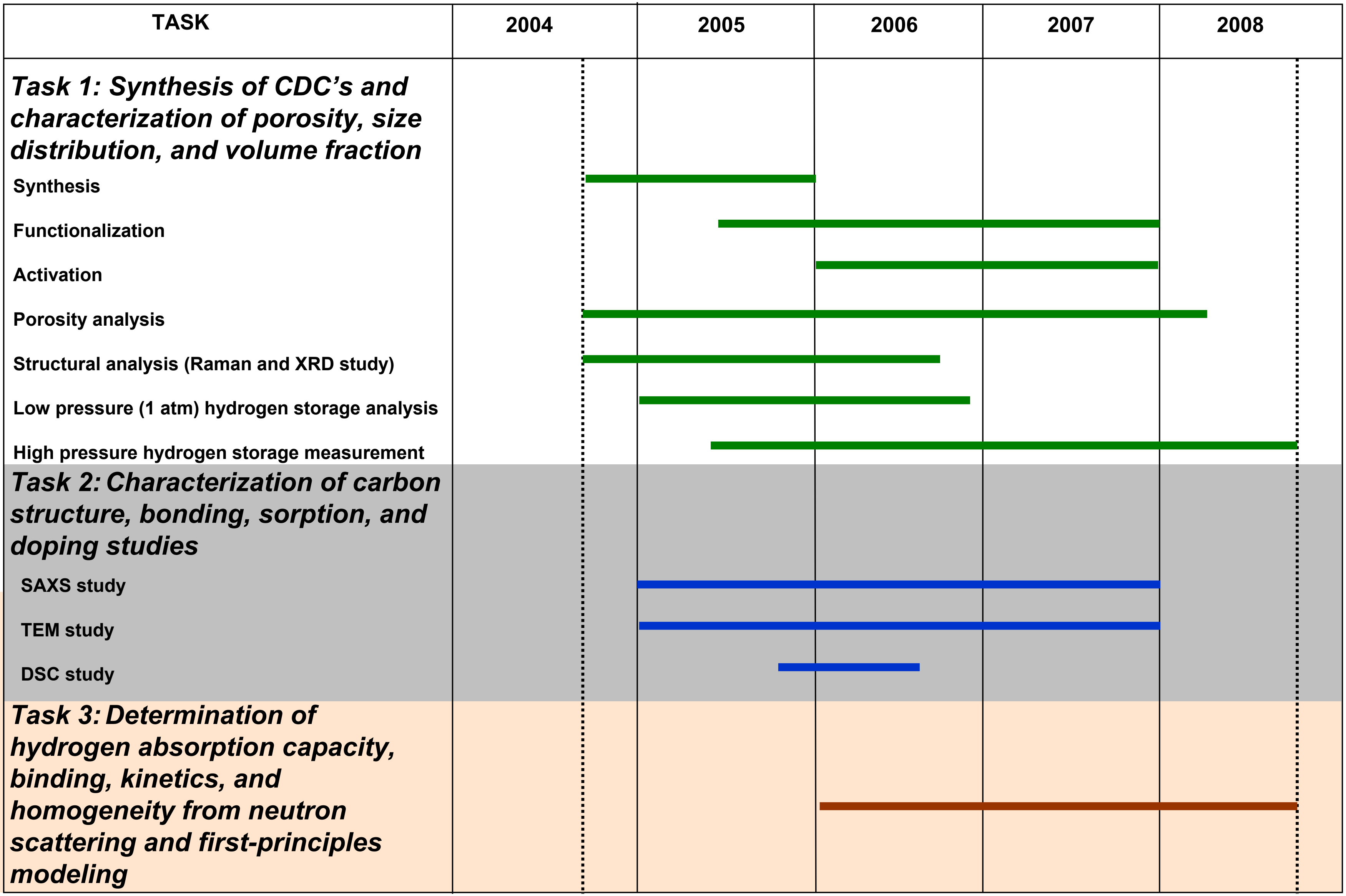
- Optimization of porosity in CDCs has a potential to meet the DOE target at low temperature and ambient pressure.

Future Work

- Study the effect of high pressure on hydrogen storage.

- Optimize CDC to achieve more than 4.5 wt.% by 2006 and 6.5 wt.% by 2008.

Summary of Program Plans



Safety

At University of Pennsylvania

The University of Pennsylvania's Office of Environmental Health and Radiation Safety (EHRS) promotes health, safety and environmental protection in teaching, research, health care and administrative activities by providing services, advice and compliance assistance. EHRS provides leadership in developing, implementing and supporting high quality programs that allows students, faculty and staff to protect themselves from hazards they may encounter at the University.

At Drexel University

The Drexel University Department of Safety and Health is responsible for the development and implementation of policies and procedures designed to create a safe workplace environment that is conducive to learning and research. Our goal is to develop compliance programs that meet and/or exceed regulatory standards and to promote standardized practices for all campuses that reduce the overall risk of injury to human health or the environment.

At NIST

The NIST reactor and experimental operations are regulated by the Nuclear Regulatory Commission. All aspects of the experimental program are rigorously reviewed by the Safety Evaluation Committee and Hazard Review Committee.

Chain of command for after hour emergencies

Health Physics: coverage to address radiation safety 24-7

Beam Experiments Coordinator: monitors neutron beam activities

Safety Officer: answers safety questions and monitors the entire facility