Project ID#: STP14

Nanostructured Activated Carbon for Hydrogen Storage

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The Polymer Research Institute of the State University of New York-esf (Syracuse) and PoroGen LLC have collaborated in an effort to develop superior high surface area nano structural carbons for hydrogen storage. Porous semicrystalline polymer with nano size pores, uniform pore size distribution, and high surface area has been developed to be a precursor to carbon. The polymer material has been tailored to form activated carbons with **slit-like micro porous** structure and high surface area. The high surface area of the polymer precursor aids in preparation of high surface area carbon, and enable doping nanostructured carbon material with chemical agents (which introduce specific interaction sites that increase the hydrogen storage capacity) .

Overview

Timeline

- Start - May 2005
- End - April 2009
- 16% Completed

due to DOE's budget reduction

Barriers

- Polymer compatibility
- Controlled doping
- High temperature tests

Budget

*Total project funding
  – DOE - $1,543,420
  – Cost Share: $391,767 (20%)
*Funding received in FY 2005
  – $80K
*Funding for FY 2006
  – $150K

Partners

PoroGen (Boston MA)

Project Objectives

Overall

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage materials with capacity 50 g H_2/L materials-based volumetric capacity, with potential to meet DOE 2010 system-level targets.

FY2005

(1) Prepare and characterize nanostructure PEEK derivatives. (2) Initiate the production of nanostructure activated carbon for hydrogen. (3) Develop methods for organometallic-doped PEEK/carbon

Technical Approach

Processing the PEEK.

Processing the PEEK/PEI precursor at high melt shear rates further controls the morphology and orientation of crystalline regions.

Hydrogen Storage (Physisorption & Chemisorption)

Prepare carbon and activated PEEK-carbons, determine the storage characteristic, pore size distribution, high ultramicropore volume, and high ultramicroporosity prepared with various activation agents.

Physisorption in carbon/PEEK: conduct H_2 , N_2 and He adsorption measurements. Study and correlate ***surface area, ultramicropore volume, pore size distribution*** and ***storage*** to the **methods of the carbon synthesis,**

Chemisorption Study methods of incorporating reactive sites into the pores of active carbon/PEEK (to promote increase in hydrogen sorption). Investigate organometallics and metal hydrides doped carbon.

Technical Approach

Activation of PEEK Carbon

Carbonization
PEEK, 320 °C, air, 15 h
→ 700 °C, N_2, 2h.

→

Mixing
grinding **Carbon/activation agent** powder in the presence of hexane

Activation
700-800 °C,
N_2, 1-4 h.

→

Wash
DI water → 1 N HCl → DI water Until pH ~ 7

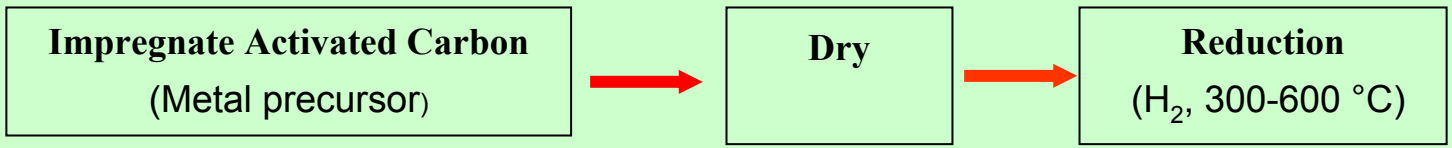
→

Dry
Vacuum, 80 °C
12-24 h.

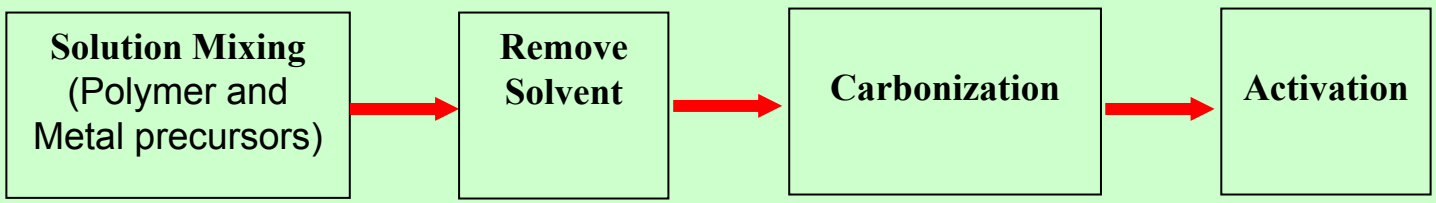
Technical Approach

Metal Doping Procedure

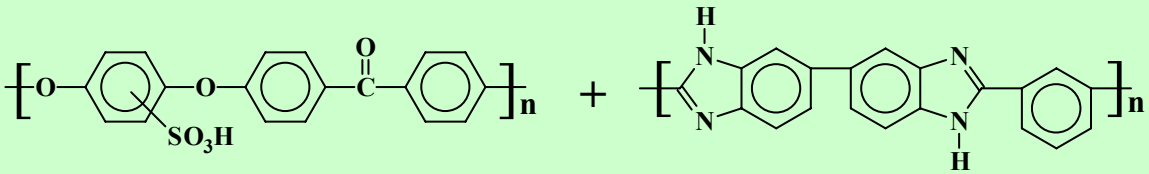
Method A



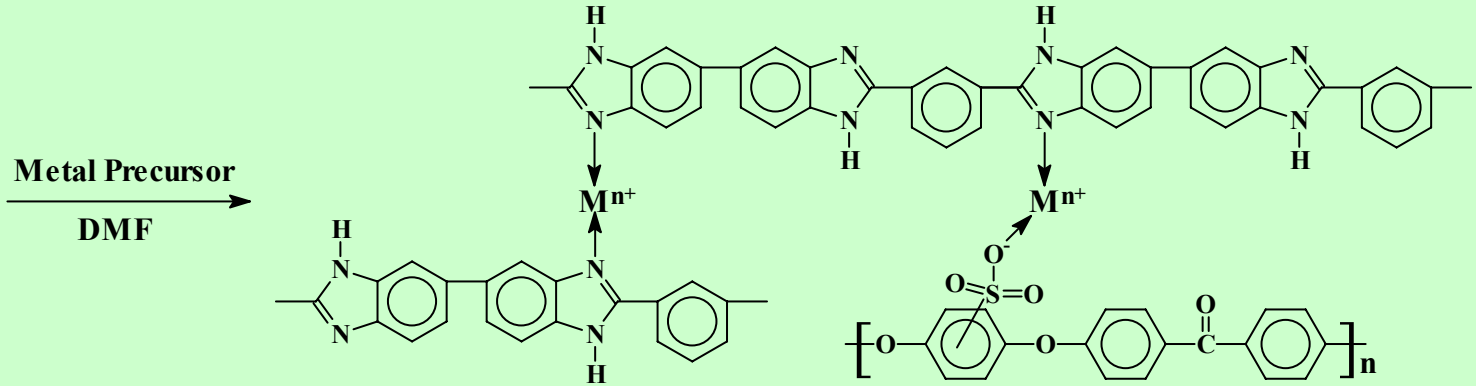
Method B



Metal-doped Carbon



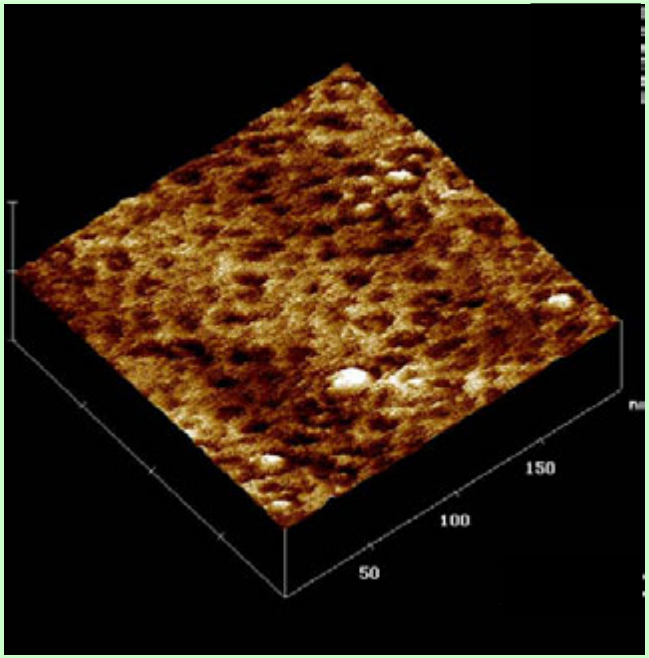
Sulfonated PEEK + PBI



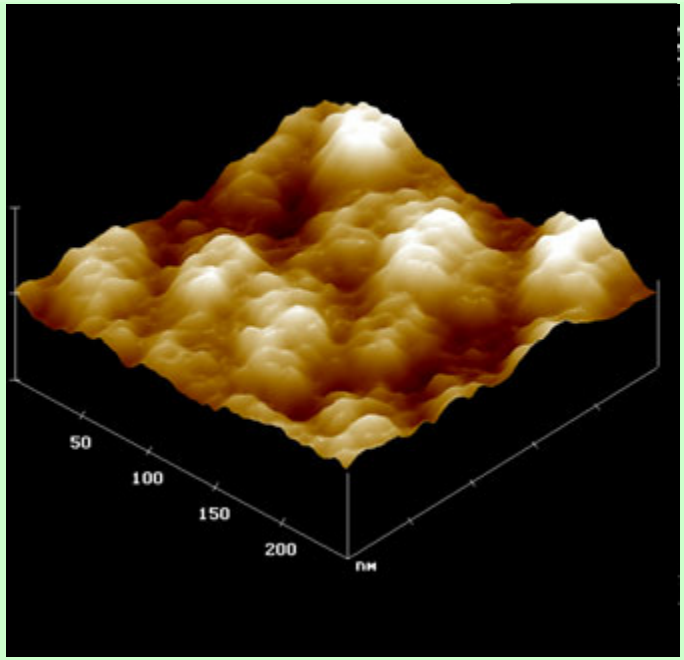
700 °C, 2 h, N_2

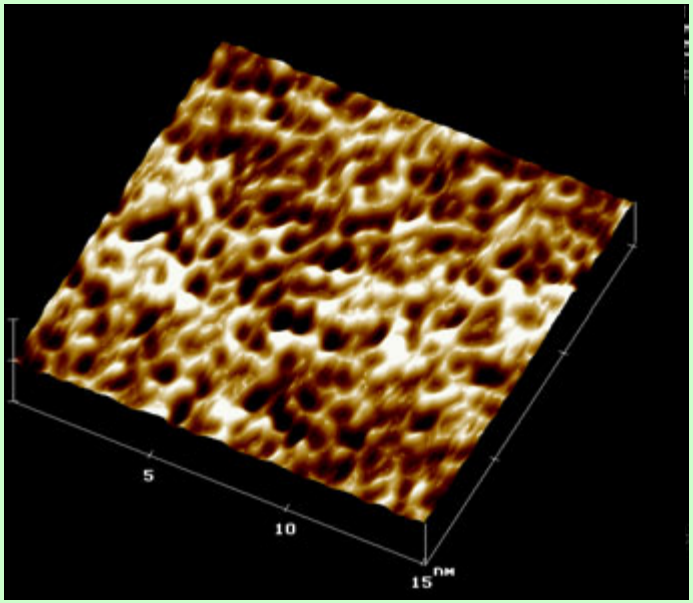
Carbonization

Metal-doped Carbon



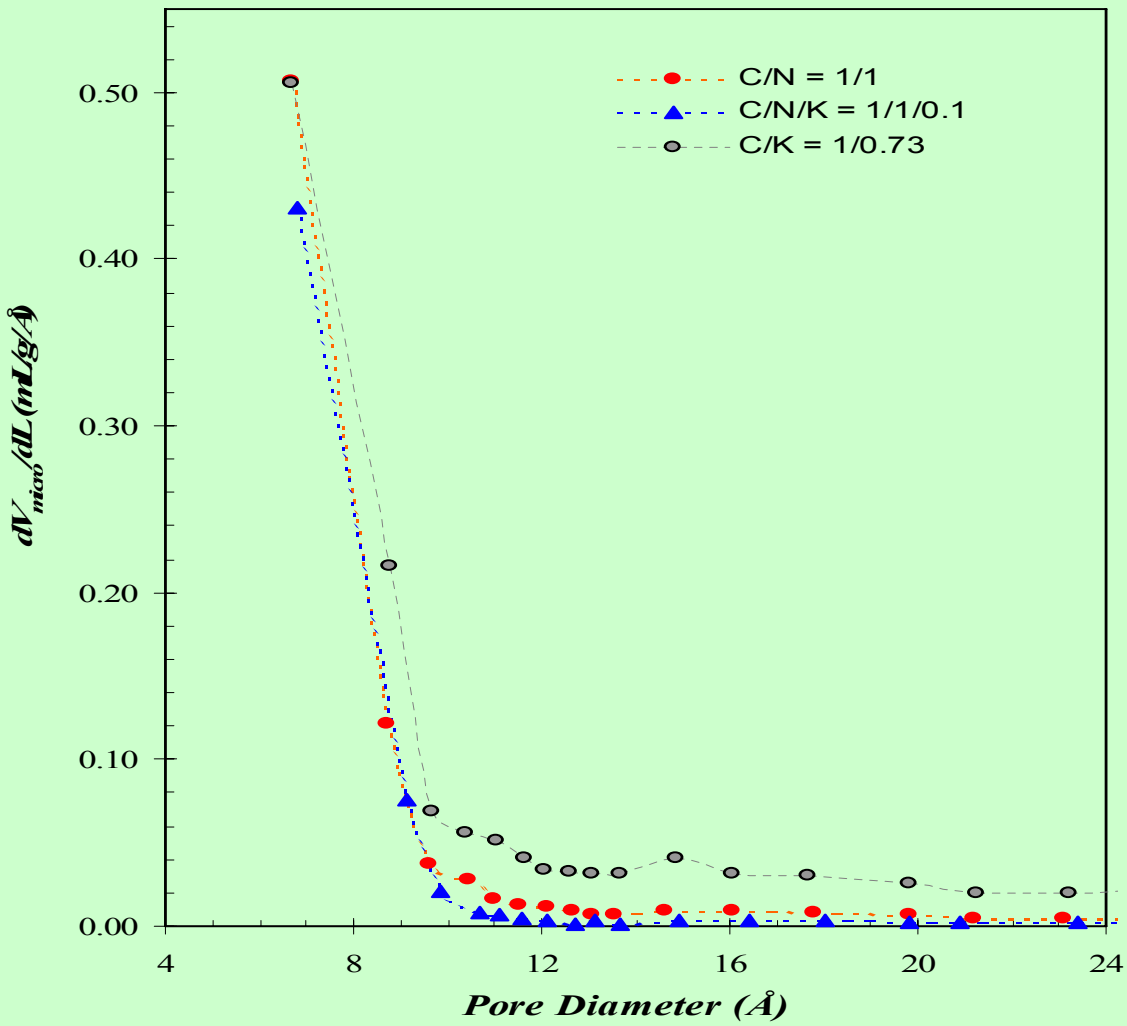
Carbonization



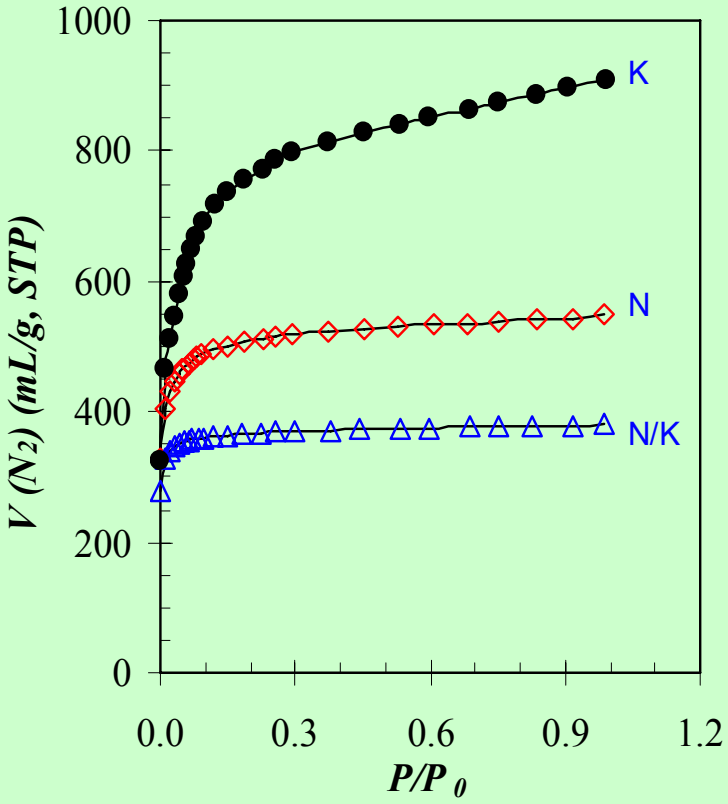


Activation

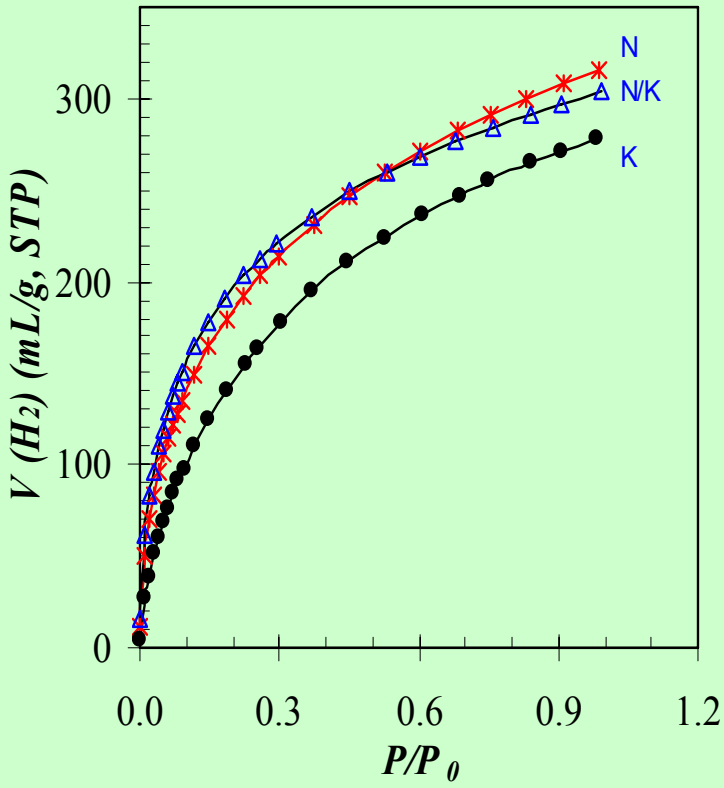
AFM images of nanoporous PEEK membrane (pore diameter ~ 16 nm), carbonized PEEK and activated PEEK carbon with average pore diameter ~ 15 Å and specific surface area ~ 3110 m^2/g.



Pore size distribution of activated PEEK carbons with high ultramicropore volume and ultramicroporosity obtained with three different N, K, and N/K co-activation.

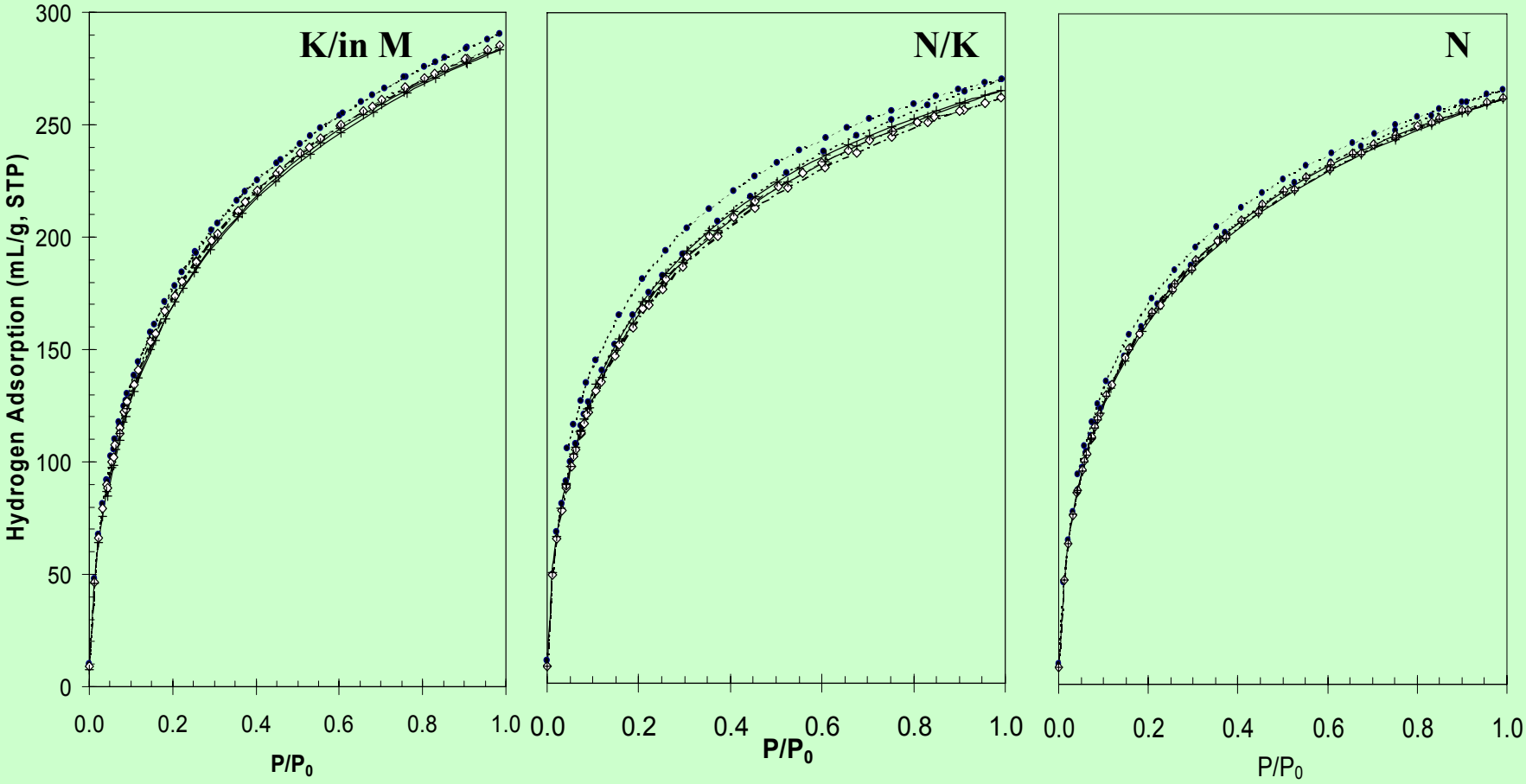


(a)



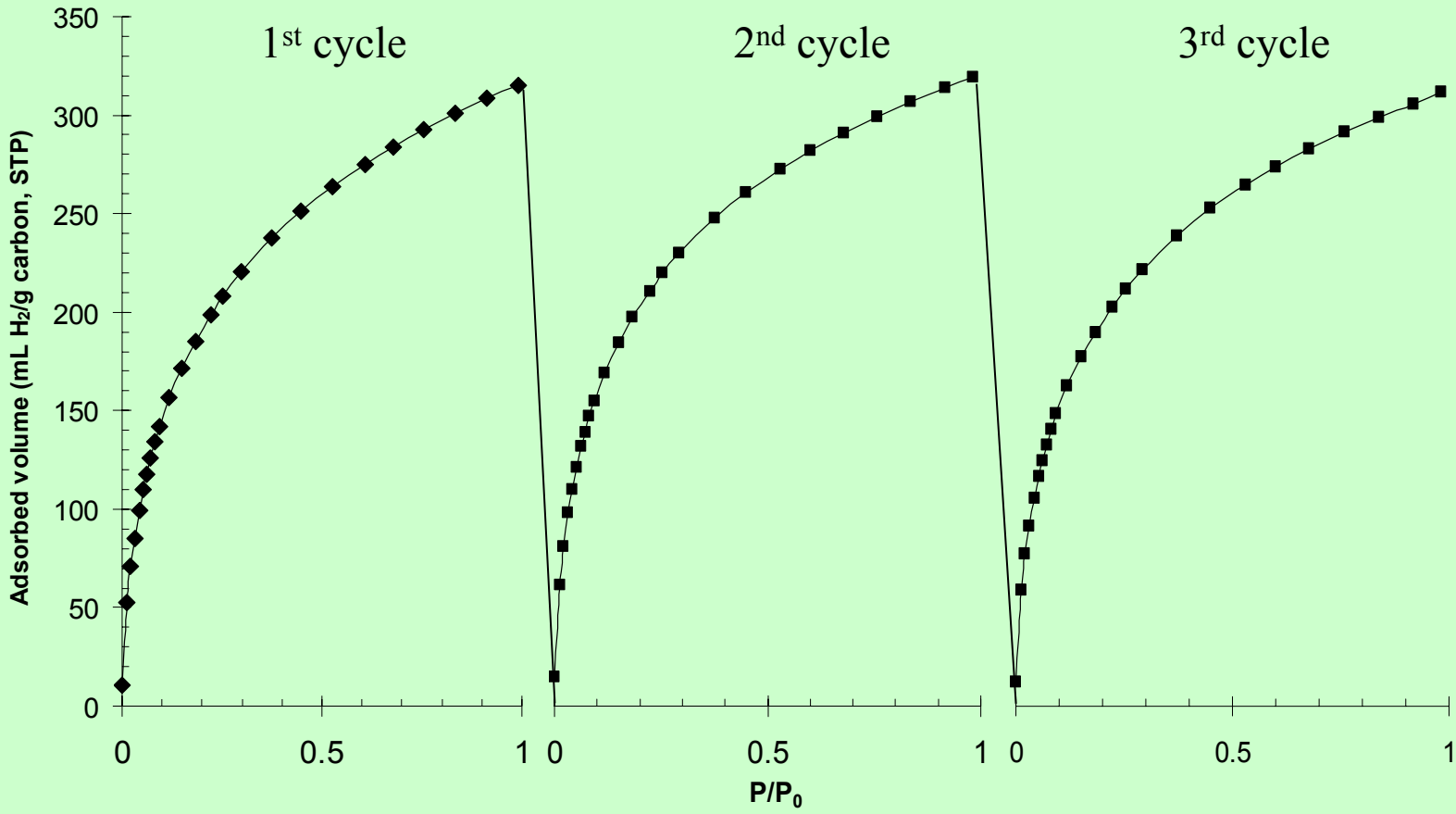
(b)

Nitrogen adsorption (a) and Hydrogen adsorption (b) isotherms of N. K, and N/K-activated PEEK carbons with S_{BET} = 1645, 2870, and 1428 m^2/g, respectively The figures show that the carbons with lower surface areas (but tailor made ultra-porosity) have higher hydrogen storage capacity..

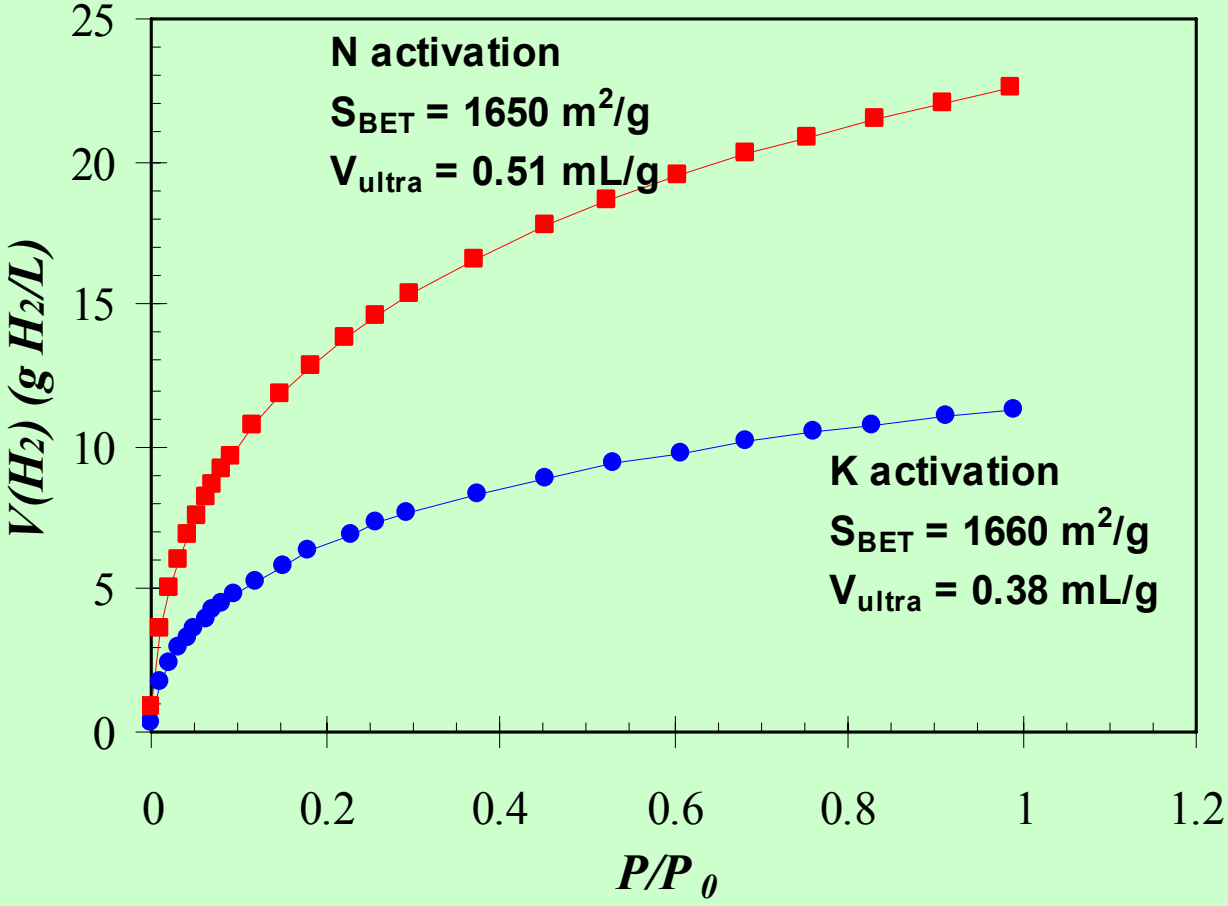


Multiple cycles of hydrogen adsorption/desorption isotherms (at 77 K) of PEEK-carbons activated with different agents K/M, N, and N/K.

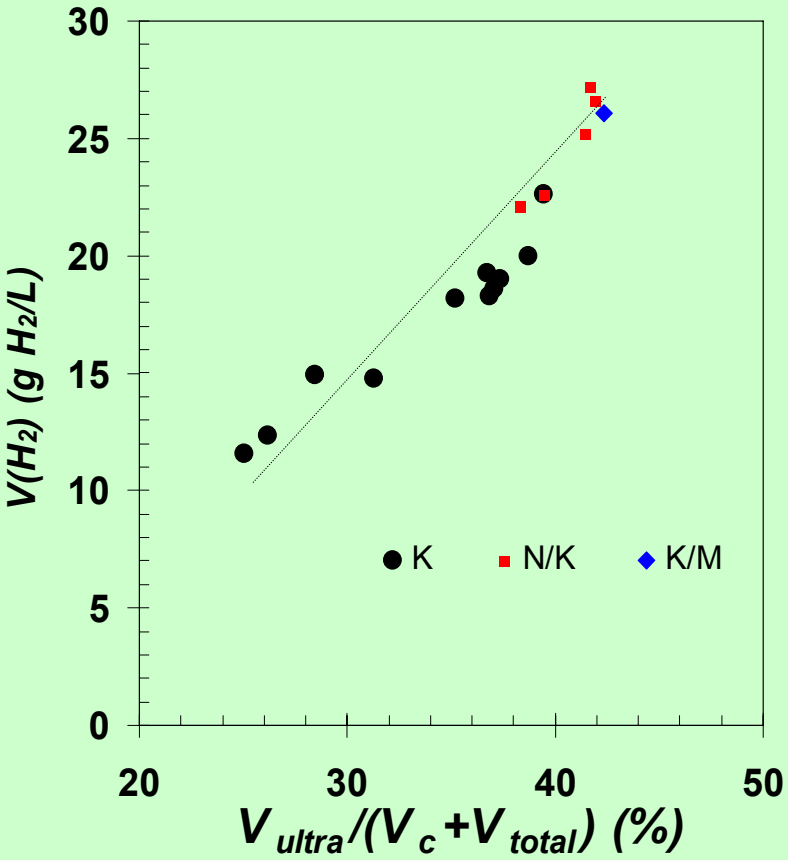
This is part of an ongoing study in optimizing activation conditions.



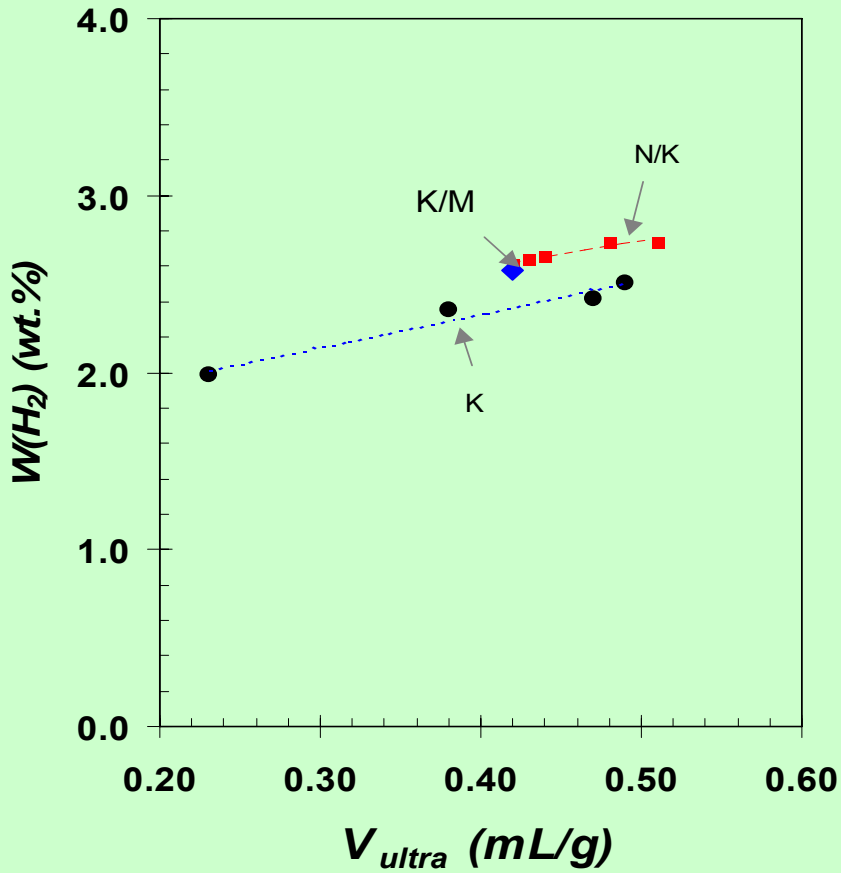
Multi-cycle test of hydrogen adsorption of N/K-activated PEEK carbon at 77 K and 1 bar. Carbon sample was desorbed under vacuum ~ 0.015 mmHg for 2 h at 200 °C. The results demonstrate that activated PEEK carbon fully retains its hydrogen storage capacity (27.5 +/- 0.02 wt%).



Volumetric hydrogen storage capacity (77 K) of PEEK carbons having similar surface area, but activated with different agents, resulting in different ultra-micropore volume.

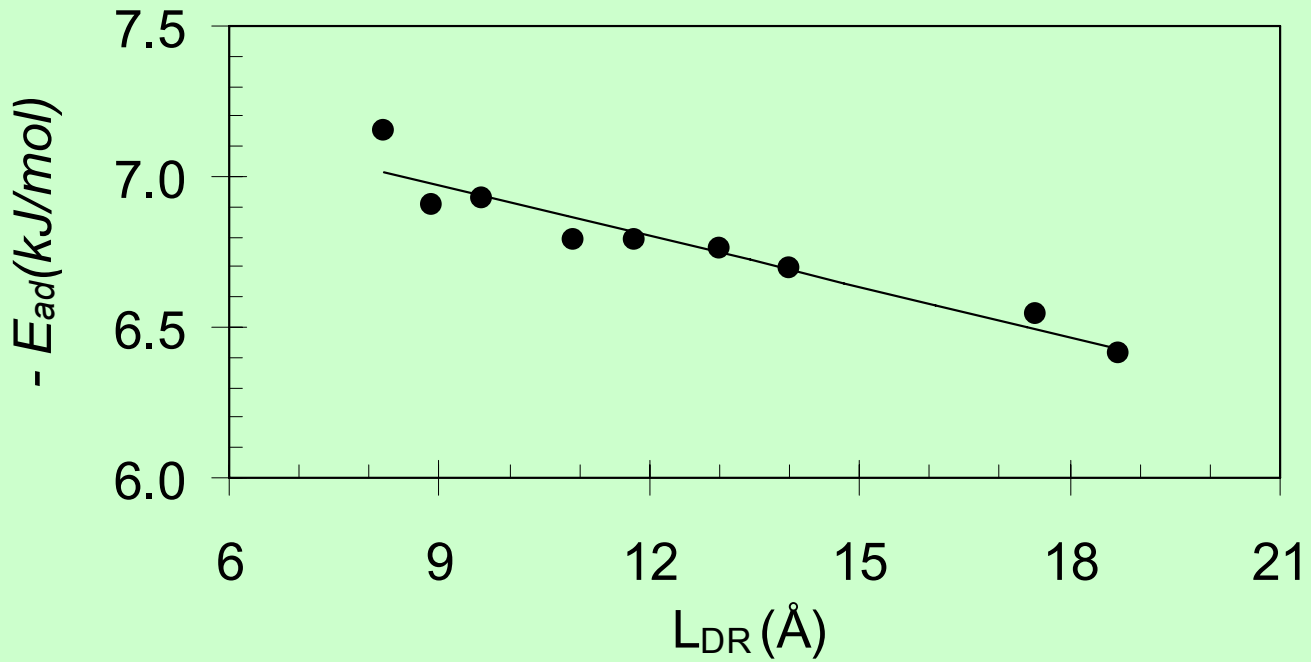


(a)

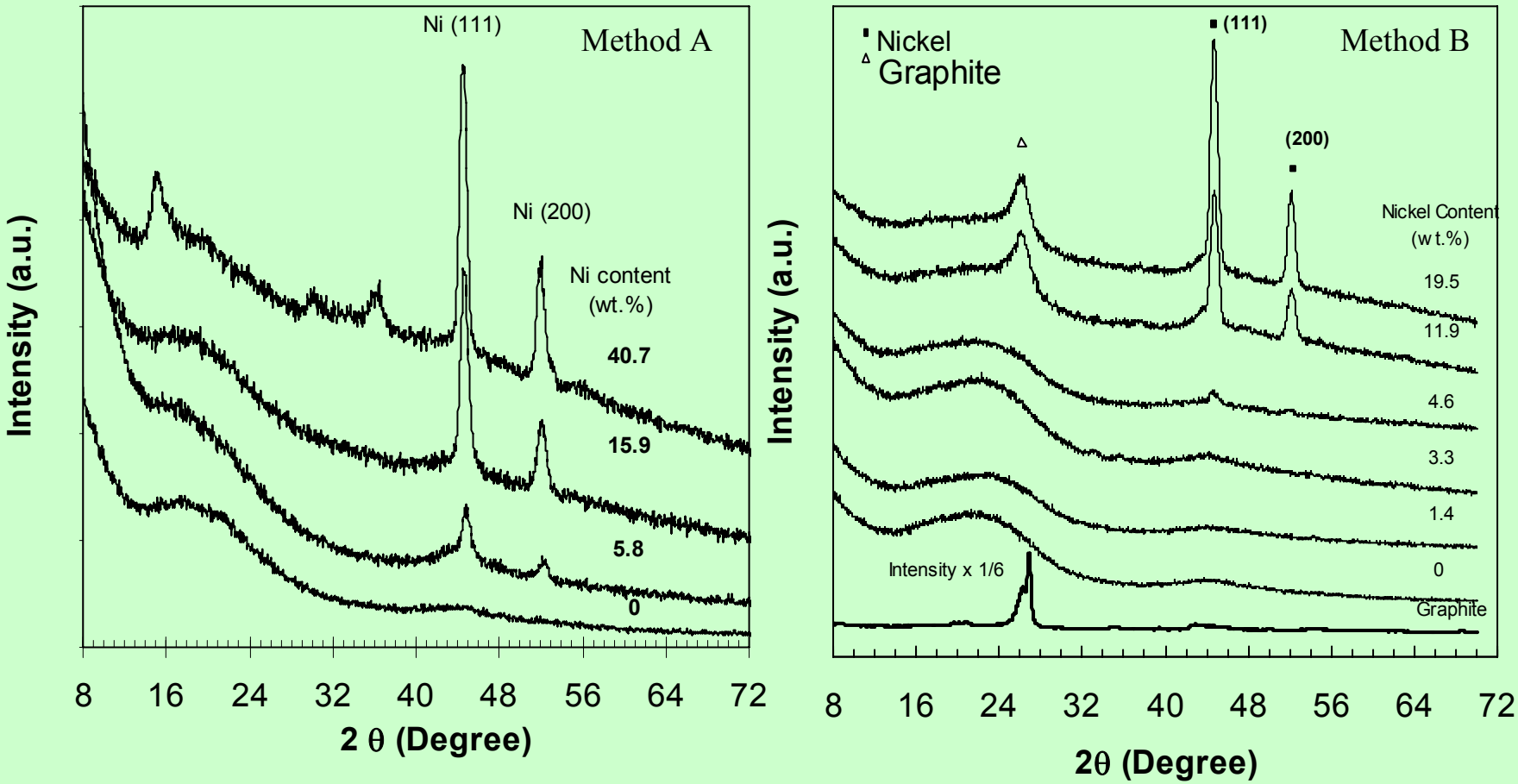


(b)

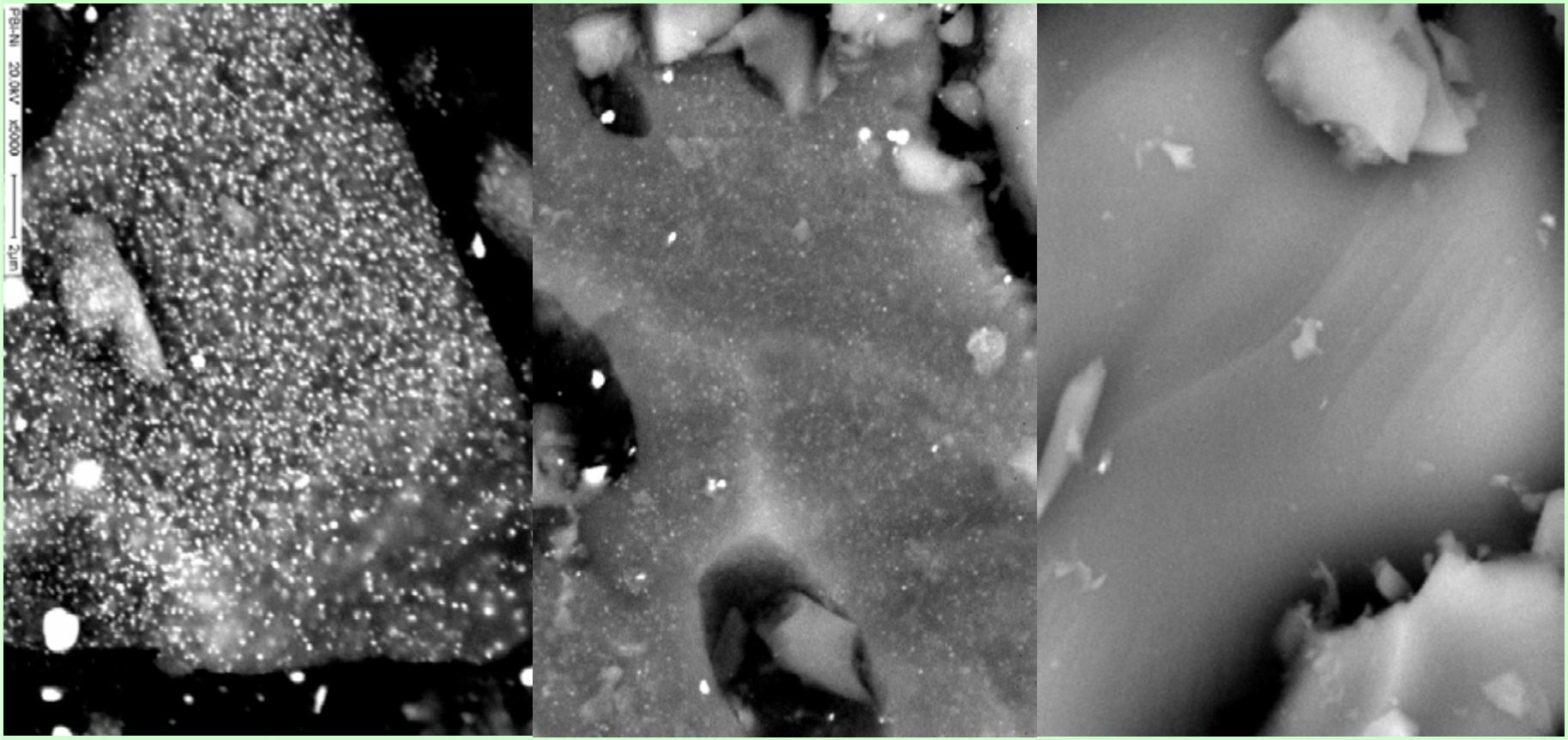
As part of the research activation agents' capabilities, Volumetric (a) and Gravimetric (b) hydrogen storage capacity of PEEK carbons activated by K, N/K and K/M agents. Volumetric storage capacity ~ 27 g H_2/L carbon [gravimetric capacity ~ 2.75—2.85 wt.%] are shown with N/K and K/M activation.



Thermodynamic study of hydrogen adsorption of activated PEEK carbons at 77 K and maximum fractional coverage. The data show that (1) hydrogen adsorption is Physisorption, and (2) reducing pore dimension leads to linear increase of hydrogen adsorption energy, thus increasing hydrogen adsorption.



Wide-angle X-ray diffraction patterns of PEEK-PBI carbons metal-doped by two different doping methods A and B.



(a) **(b)** **(c)**

Back-scattering SEM micrographs of: 20 wt% metal-doped (a), 5 wt% metal-doped (b), and non-doped (c) non doped PEEK carbons

(all samples are of pre-activated carbon)

Planned work for FY06-FY07:

- Continue to develop, modify and characterize nanoporous **PEEK/blend** materials and carbons.
- Continue study of activation agents for the production of nanostructured carbon; characterization of the products via low and high pressure H_2, N_2, and He sorption tests.
- Develop methods of doping blend-**PEEK** carbon with metal hydrides (e.g., MgH_2 and $RSiH_n$) transition metals (Ti, Ni, V) and organometallic compounds.
- Characterization of doped activated carbons
- Elevated temperature hydrogen adsorption tests of metal-doped PEEK carbons.

Summary

1. Preliminary data indicate that N type and K/M are effective activation agents to synthesize carbons with high ultramicroporosity and ultramicropore volume.

2. High ultramicropore volume (V_{ultra} ~ 0.51 mL/g) and high ultramicroporosity (V_{ultra}/V_{micro}~ 78%) have been achieved.

3. During this early stage, activated **PEEK**-carbon has been produces having gravimetric hydrogen adsorption capacity up to ~2.7-2.85 wt.%, and volumetric capacity up to 27.0 g H_2/L at 77 K, 1 bar.

4. Metal-doped carbons have been synthesized and characterized by WAXD and SEM.