

# Polymer-Based Activated Carbon Nanostructures for H<sub>2</sub> Storage

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The Michael Szwarc Polymer Research Institute of the State University of New York-esf (Syracuse) and PoroGen LLC have collaborated in an effort to develop polymer-based nano structural carbons:

- High BET surface area  $> 2600 \text{ m}^2/\text{g}$ ;
- High microporosity  $> 95\%$ ;
- Average pore size  $\sim 10 \text{ \AA}$ ;
- Hydrogen uptake:  $\sim 7 \text{ wt\%}$  and  $45 \text{ g H}_2/\text{L}$ ;
- Increasing hydrogen storage temperature by doping carbons with multicyclic ligands.

# Overview

## Timeline

- **Start - May 2005**
- **End - April 2009**
- **50% Completed (due to DOE's budget shortage)**

## Budget

- **Total project funding**
  - DOE - \$1,543,420
  - Cost Share: \$391,767 (20%)
- **Total funding received by FY 2007**
  - \$430K
- **Funding received for FY 2007**
  - \$230K

## Barriers

- **Polymer compatibility**
- **Controlled doping**
- **High temperature tests**

## Partners

**PoroGen (Boston MA)**

# Project Objectives

## Overall

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage materials with materials-based volumetric capacity of 50 g H<sub>2</sub>/L, with potential to meet DOE 2010 system-level targets.

## FY2007 - 2008

- Develop polymer-based nanostructured carbons with high surface area and high micropore volume;
- Demonstrate reproducibility of 10-gram scale batch production of high surface area carbon;
- Characterize hydrogen storage capacity under various pressure and temperature conditions. Target for 2007 > 6 wt% and 40 g/L of material-based H<sub>2</sub> capacity;
- Develop methods for organometallic and multicyclic ligand-doped polymer/carbon.

# Technical Approach

## Processing

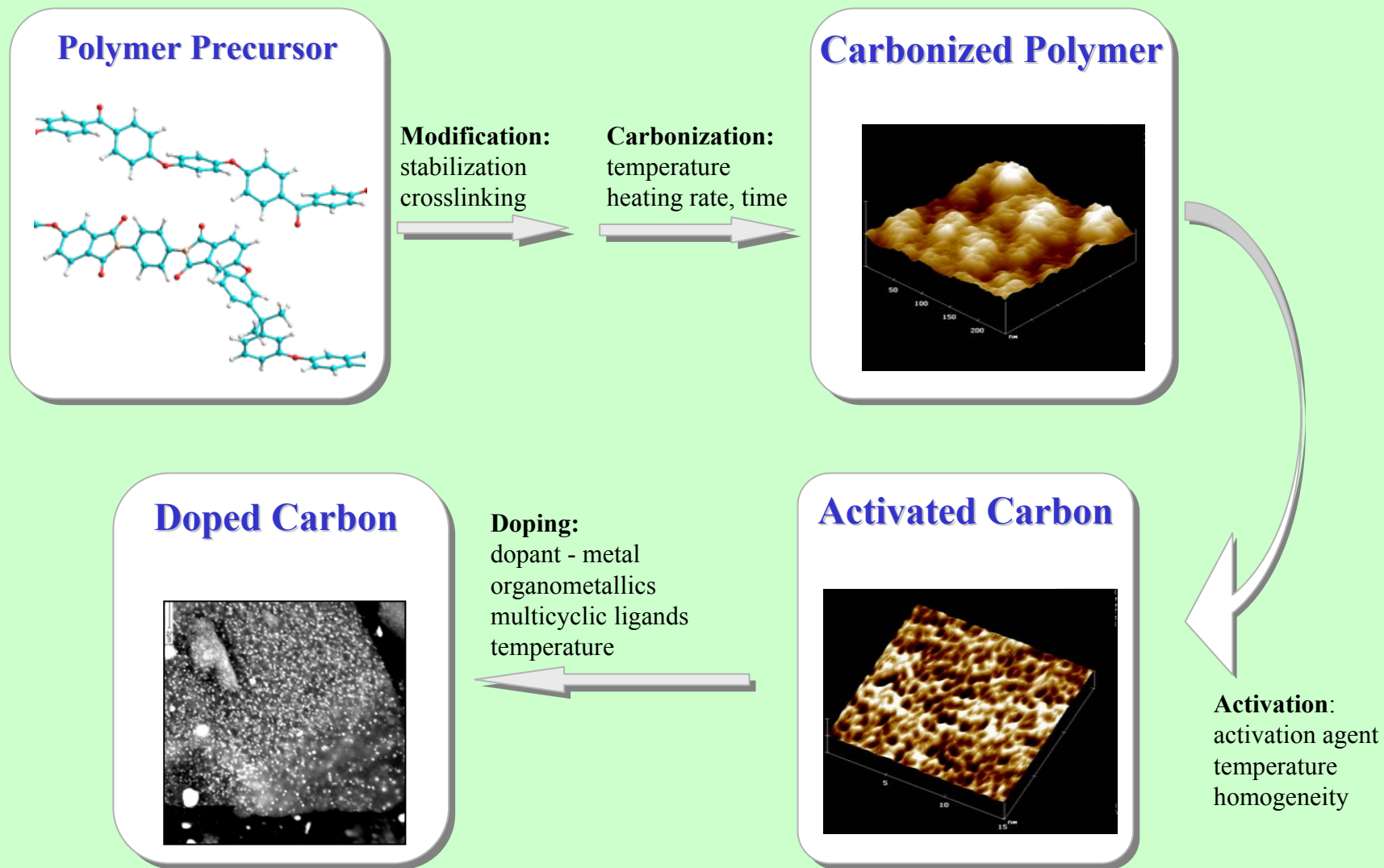
Processing the precursors (MPPO, MPEEK and PEI) at high melt shear rates further controls the morphology and orientation of crystalline regions.

**Hydrogen Storage (Physisorption & Chemisorption)** Prepare carbon and activated polymer – based carbons, determine the storage characteristic, pore size distribution, high ultramicropore volume and high ultramicroporosity prepared with various activation agents.

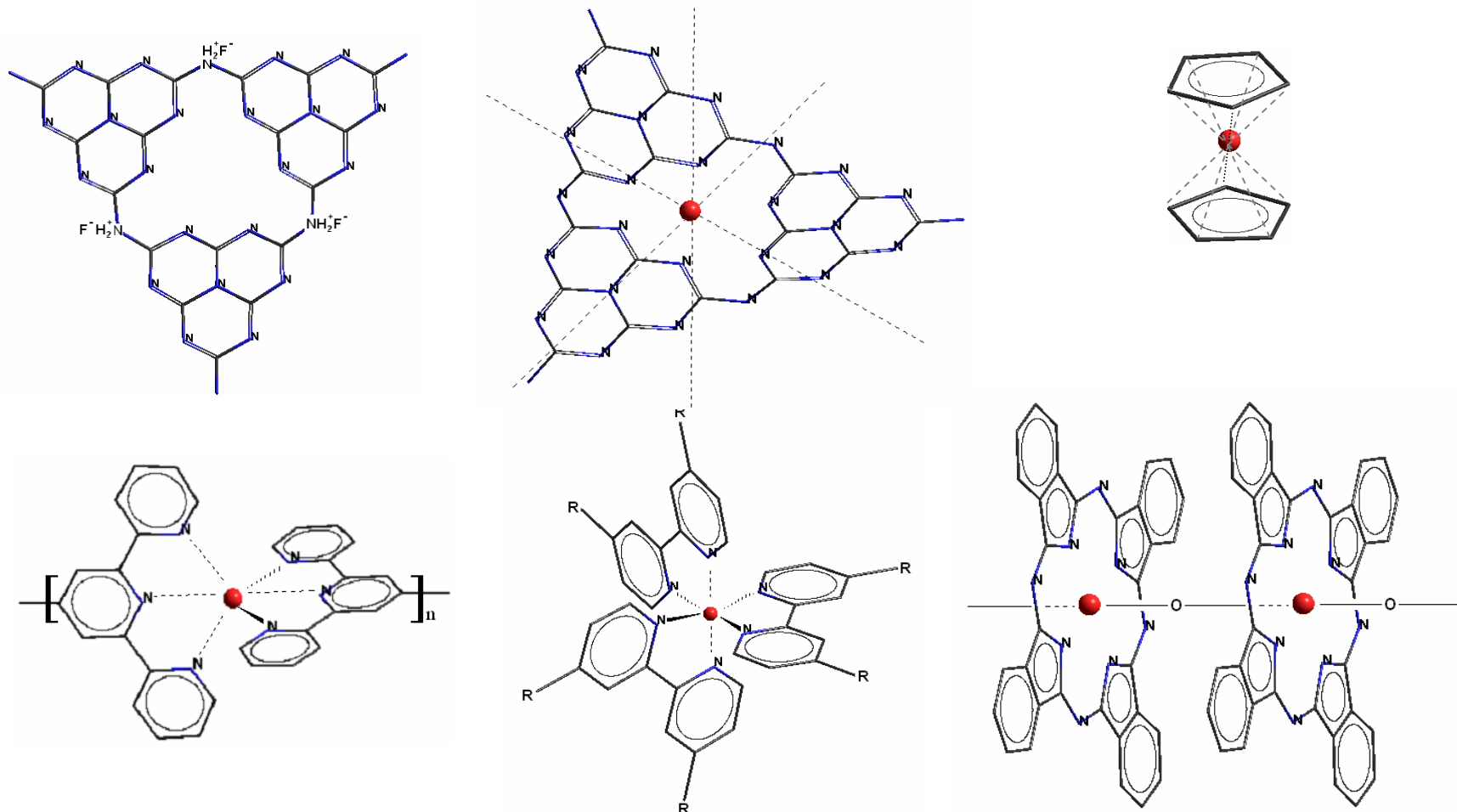
**Physisorption in carbon/polymer** Conduct H<sub>2</sub>, N<sub>2</sub> and He adsorption measurements. Study and correlate *surface area, ultramicropore volume, pore size distribution* and *storage* to the **methods of the carbon synthesis**.


**Chemisorption** Study methods of incorporating reactive sites into the pores of activated carbon/polymer. Investigate organometallics, metal hydrides and multicyclic ligand - doped carbons.

# Nanostructured Activated Polymer Carbon Preparation Methodology



# Organometallic and Multicyclic Ligand Dopants



 **Metal center (Mg, Ti, Sc, Ru, Pt and other transition metals)**

# Correlation of Surface Area with Pore Size of Activated Polymer Carbons

## Formation of porous structure

1<sup>st</sup> Stage Burn-Off: pore creation dominates → higher surface area, smaller pores;

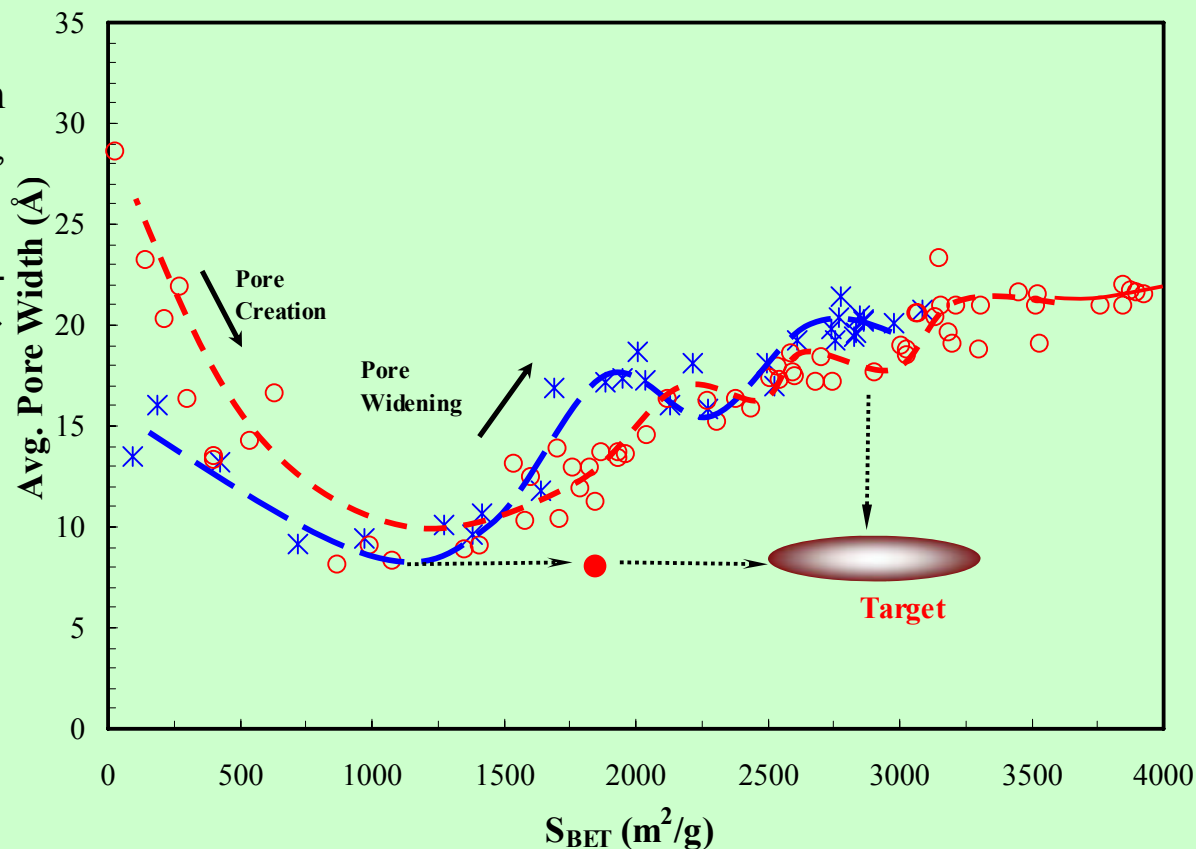
2<sup>nd</sup> Stage Burn-Off: pore enlargement and fusion dominate → higher surface area, larger pores.

### Target:

$S_{\text{BET}} > 2600 \text{ m}^2/\text{g}$  with average pore width  $\sim 8 \text{ \AA}$

### Achieved (●):

$S_{\text{BET}} \sim 1850 \text{ m}^2/\text{g}$  with average pore width  $\sim 8 \text{ \AA}$



All points represent experimental data

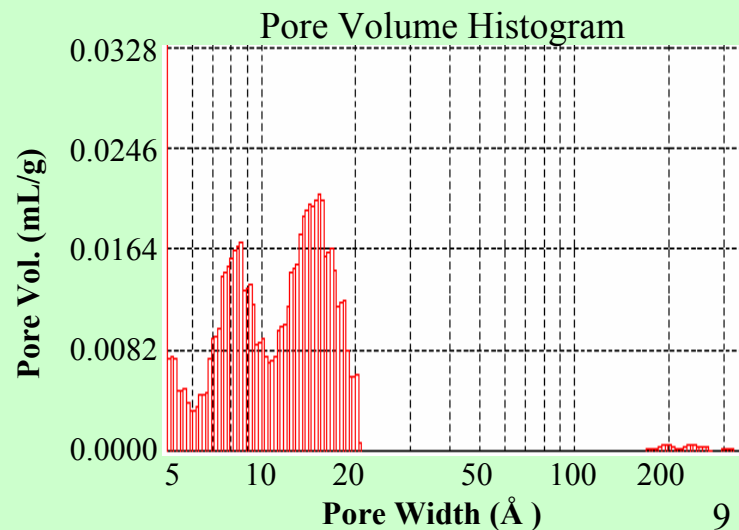
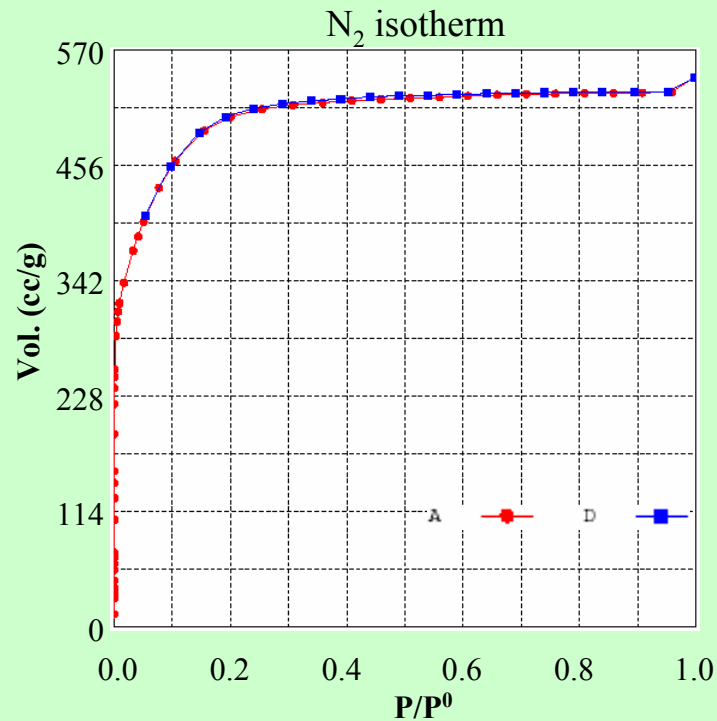
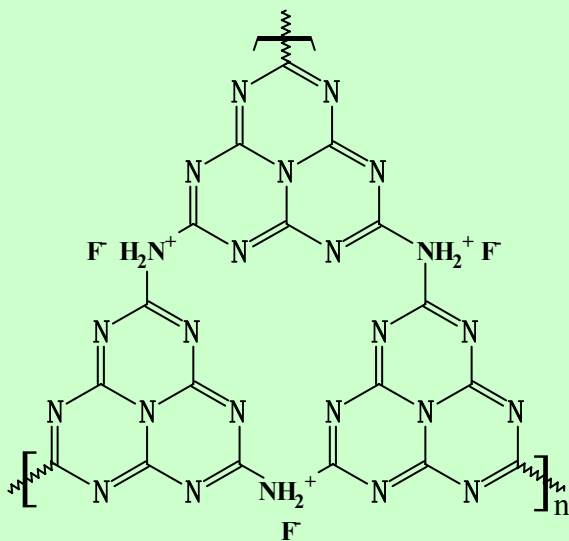


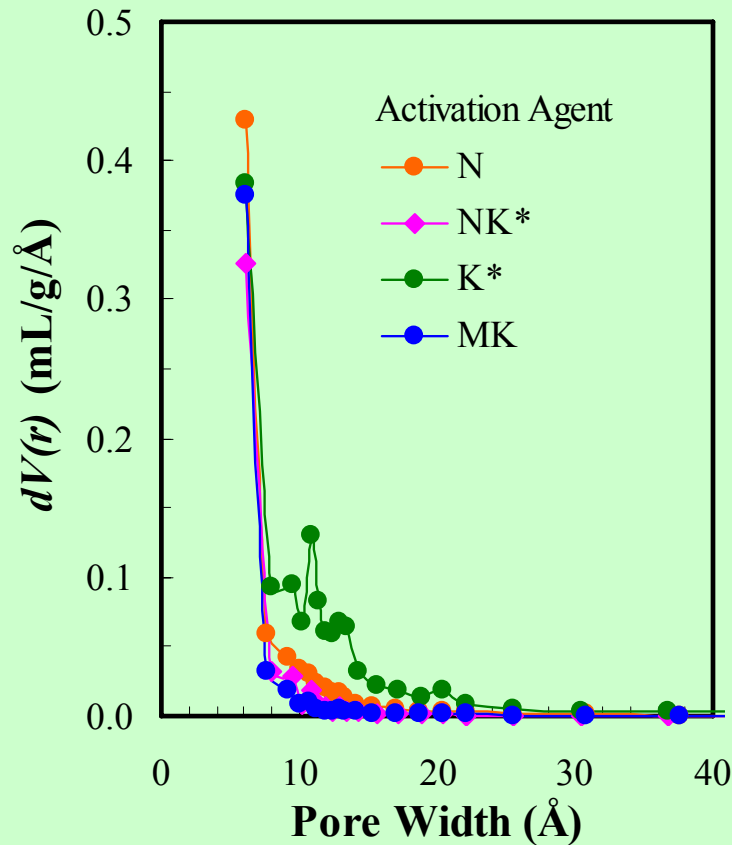
# [CNH]<sub>n</sub> doped high surface area polymer carbon

BET surface area: 1850 m<sup>2</sup>/g

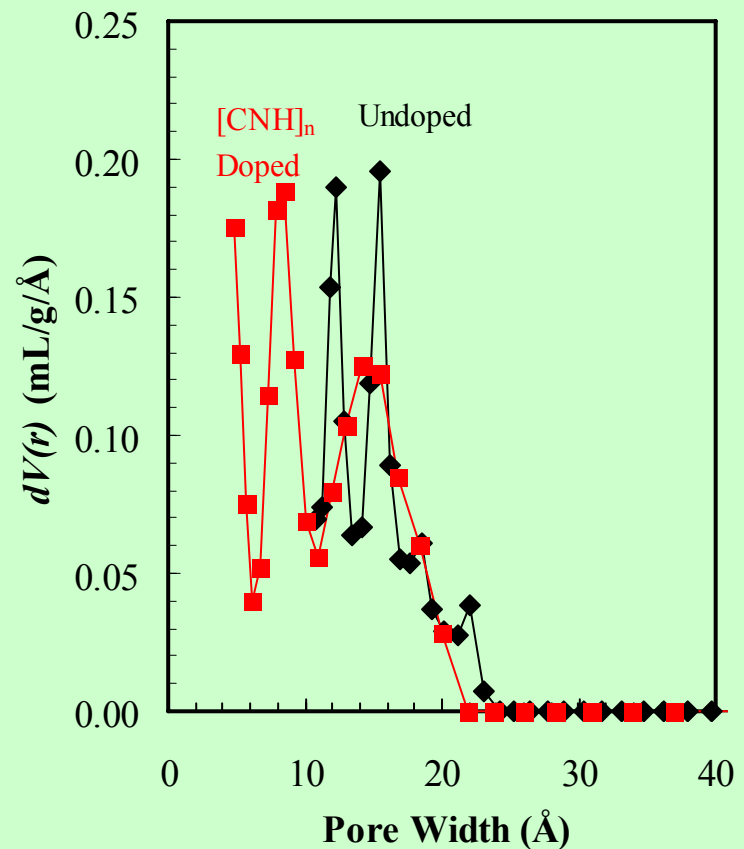
Pore Vol.: 0.84 mL/g

Average Pore Width: 8.52 Å

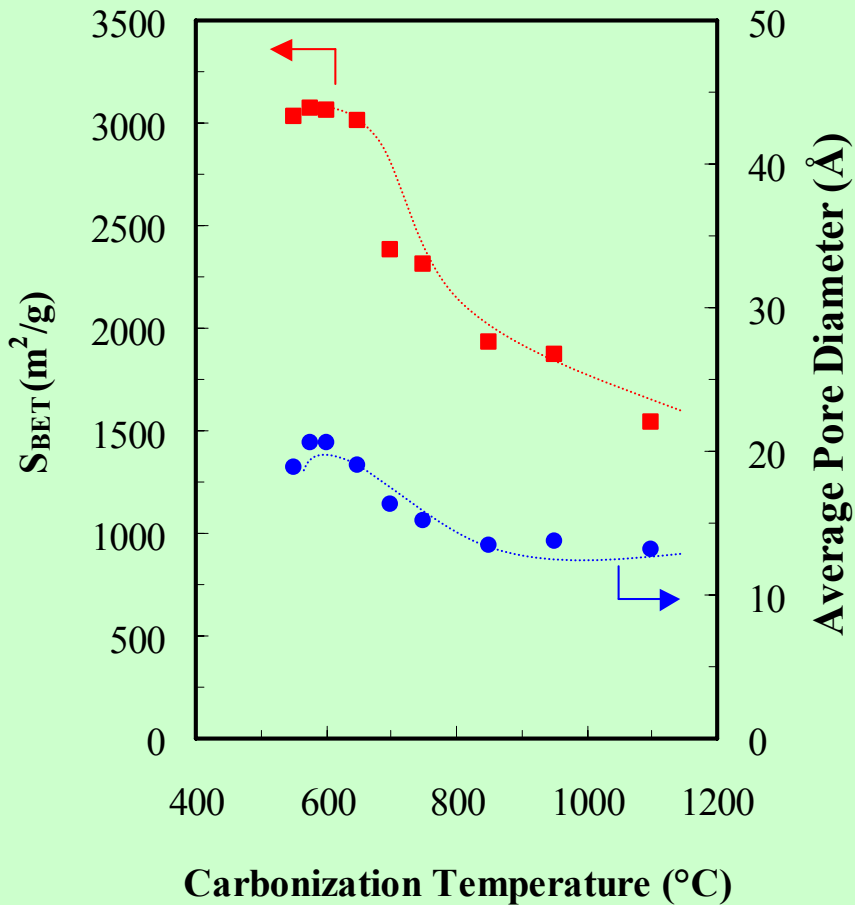




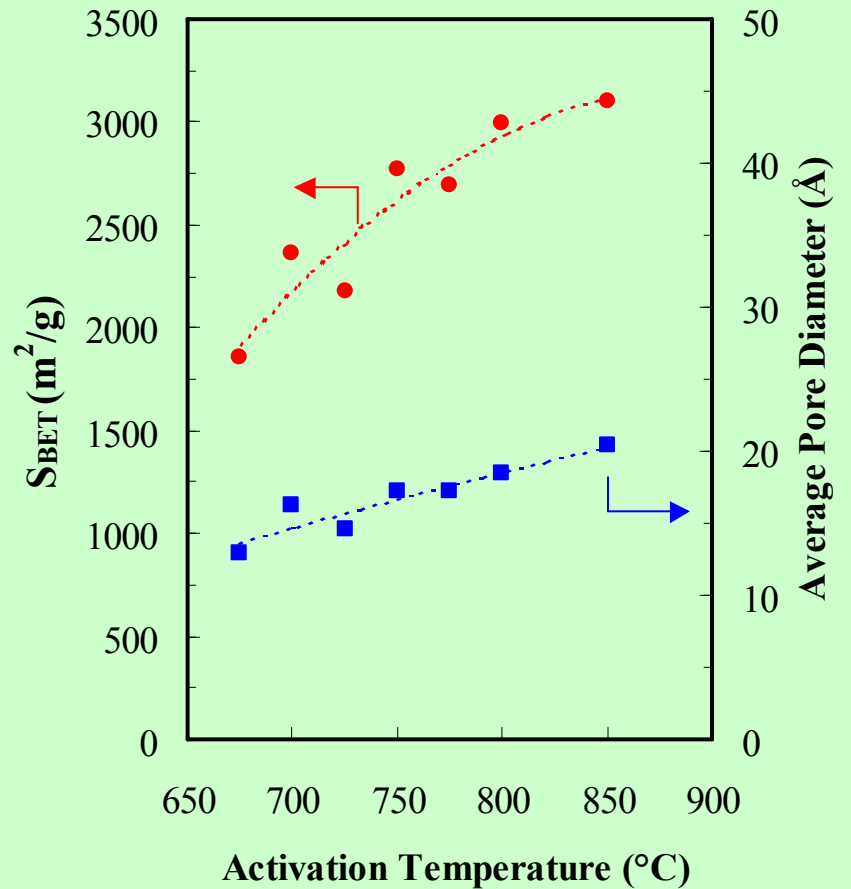
**Strategy I:** Develop a set of activation agents. Activation agent MK has a better affinity to carbon matrix, allowing homogeneous activation and, hence, narrow pore size distribution.



**Strategy II:** Doping the activated carbon with polycyclic compounds to tailor pore size and distribution. Average pore size decreases from 18.6 Å for undoped carbon to 8.5 Å of [CNH]<sub>n</sub> doped carbon.

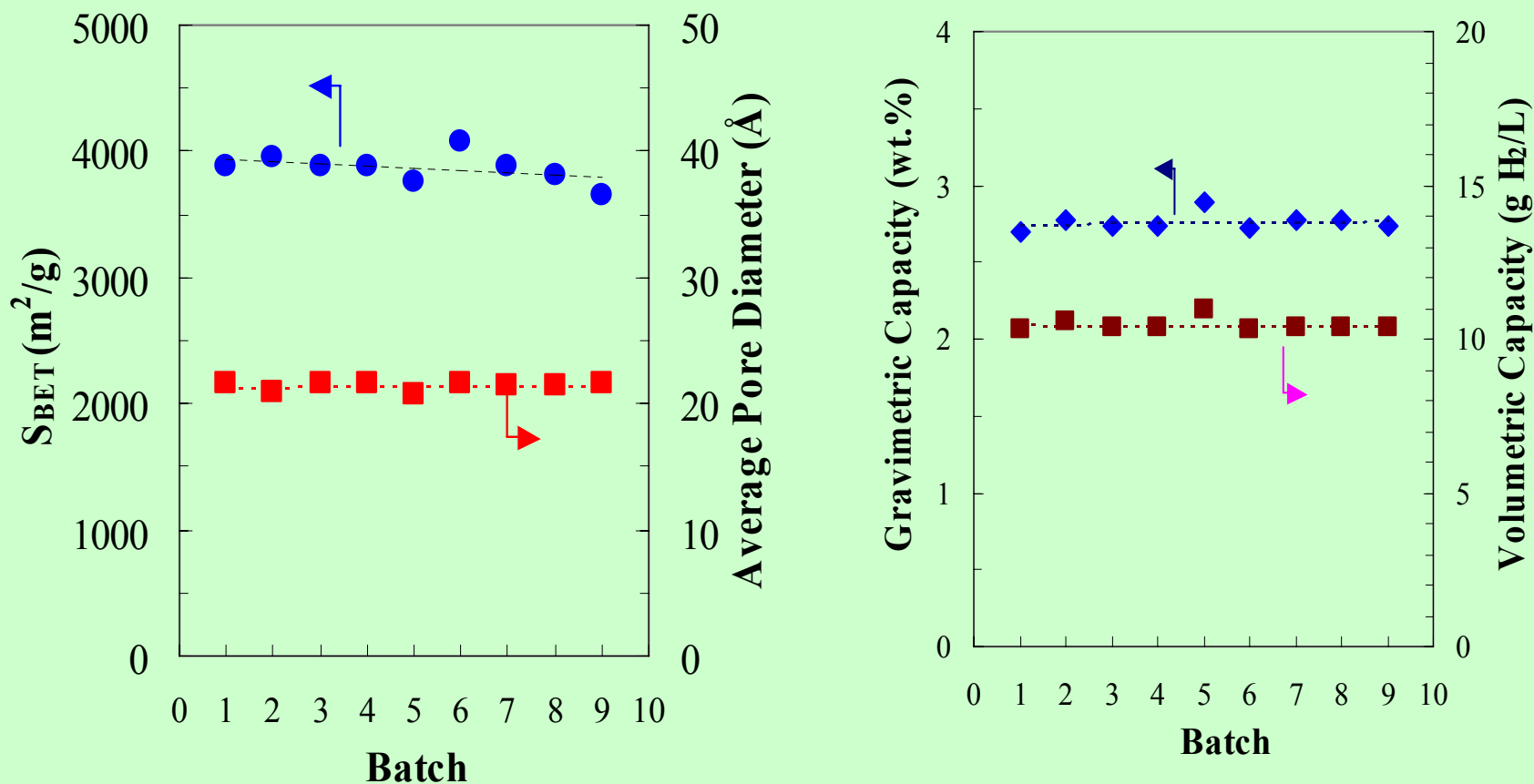


**Strategy III:** Adjusting carbonization temperature. Carbonization at 600-800  $^{\circ}C$  achieves the desired pore diameter and surface area.

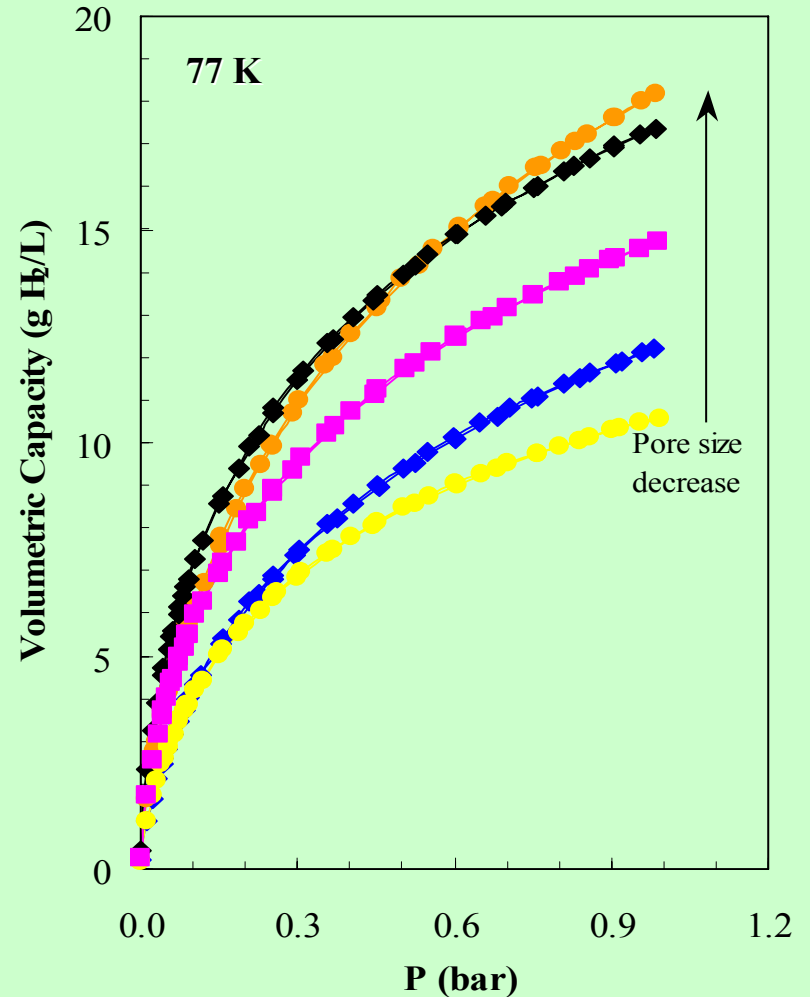
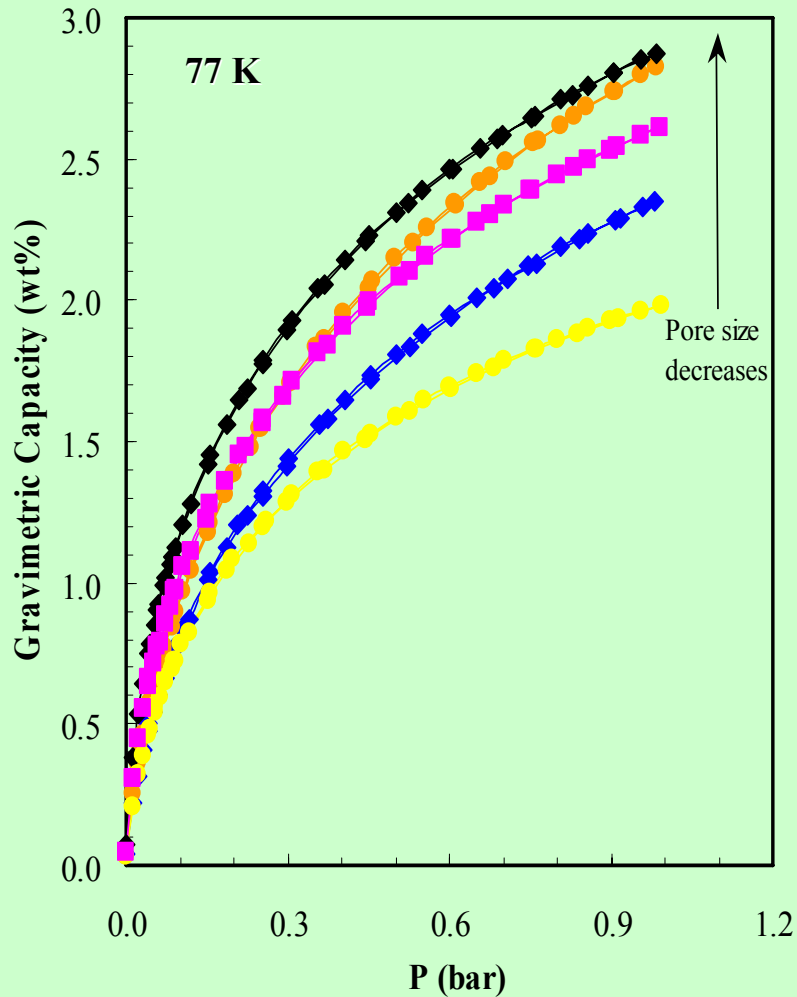


**Strategy IV:** Adjusting activation temperature to achieve the desired pore diameter and surface area.

# Reproducibility of the Production of Activated Polymer Carbons

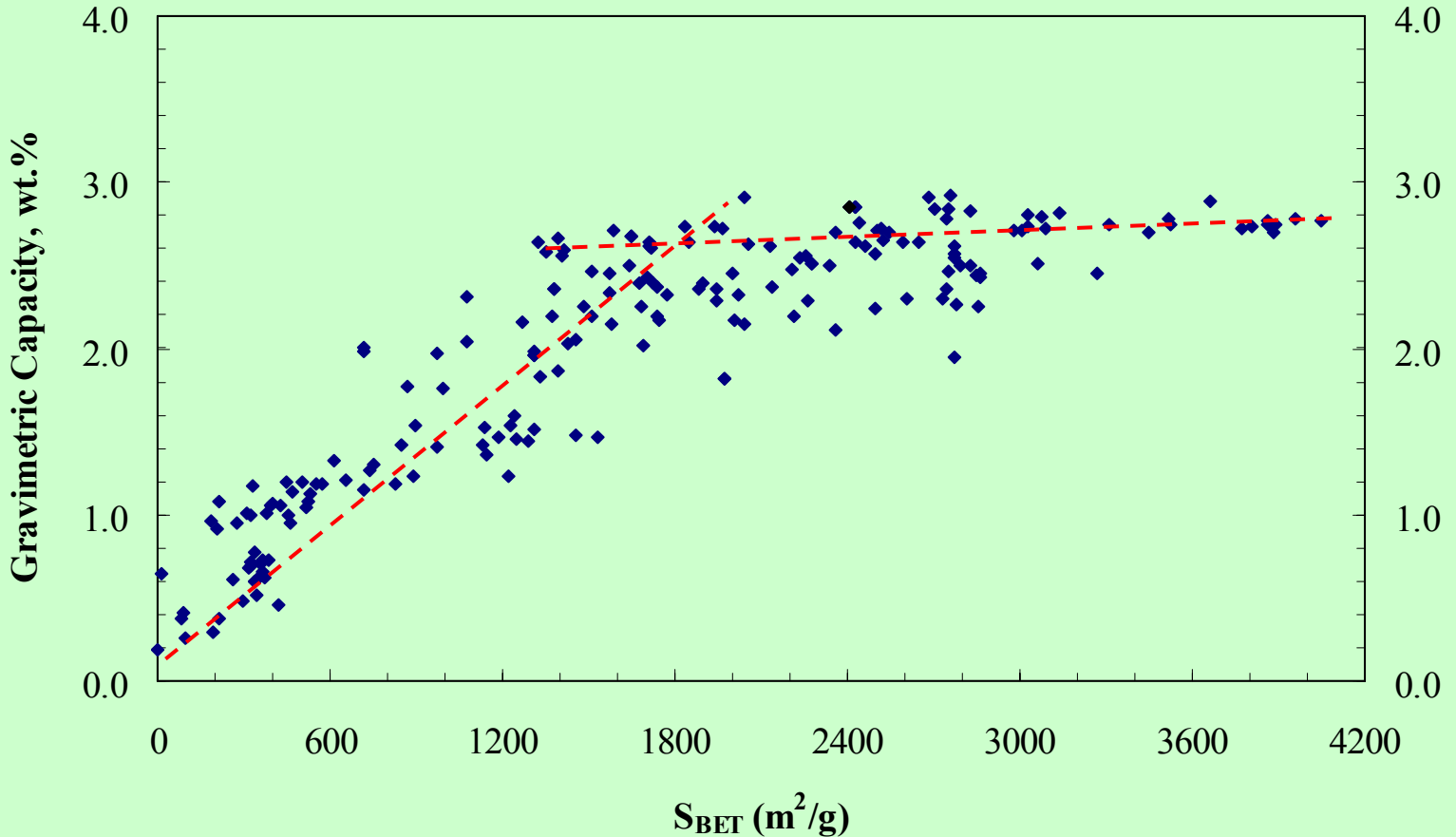


10-g batch synthesized carbons shows a variation of surface area  $\pm 2.4\%$  and hydrogen capacity  $\pm 2.0\%$  at 77 K and 1 bar.

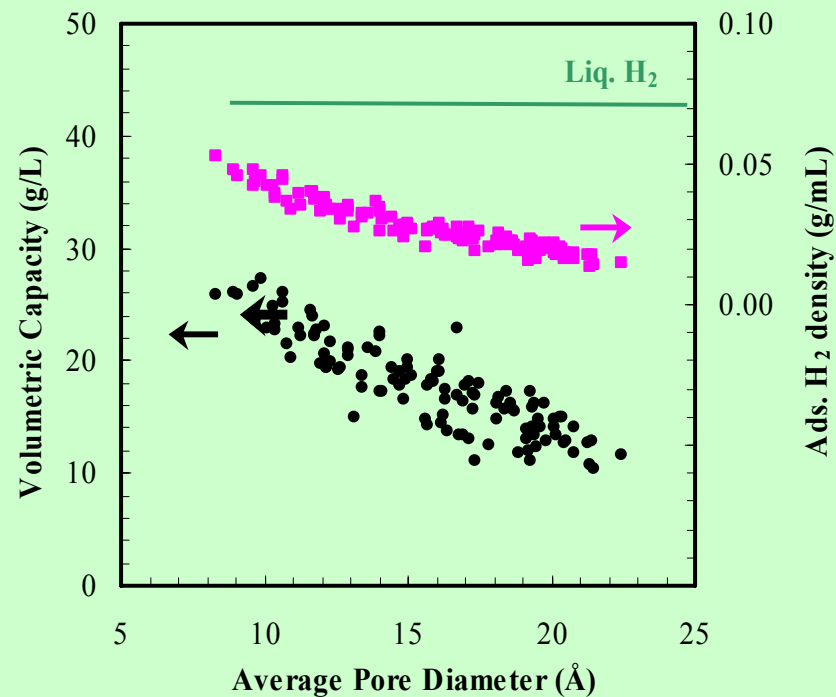
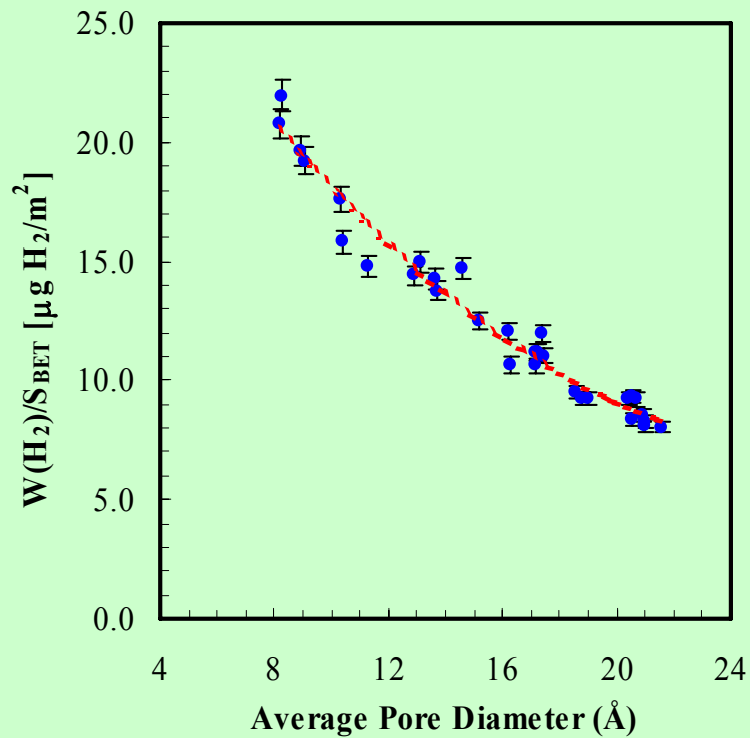


- Hydrogen sorption is reversible at 77 K and pressure up to 1 bar;
- Gravimetric and volumetric capacity both increase as average pore size decreases from 22 to 17 Å. (All carbon samples shown in the figures have a similar BET surface area of  $\sim 2700 \text{ m}^2/\text{g}$ );
- Small pore size is essential for high hydrogen storage capacity.

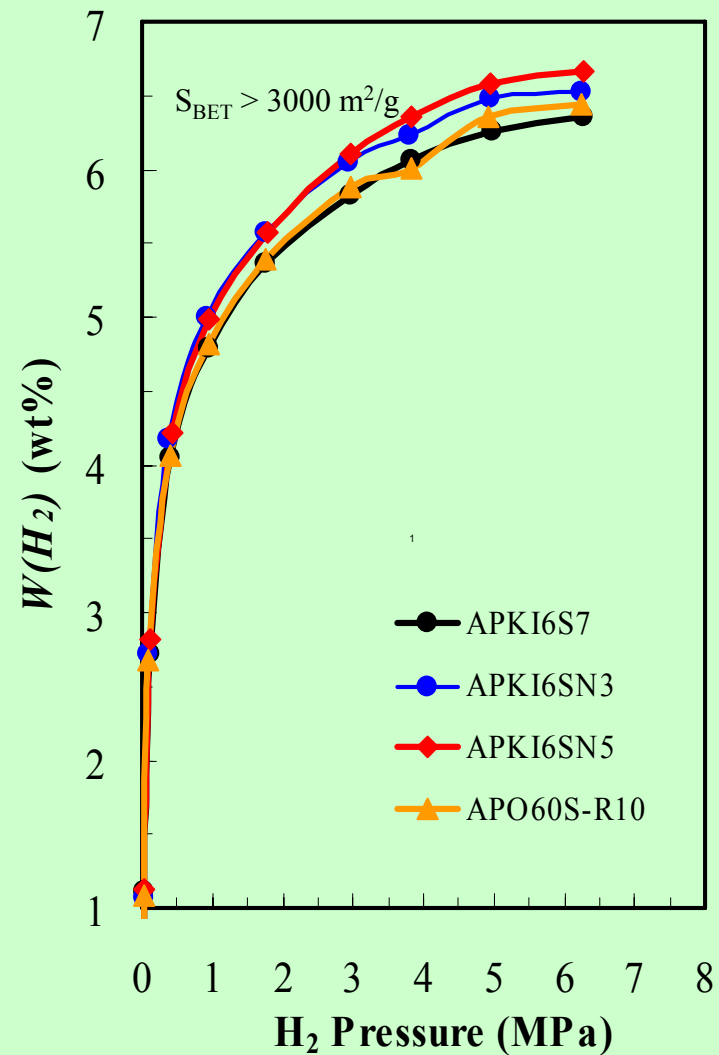
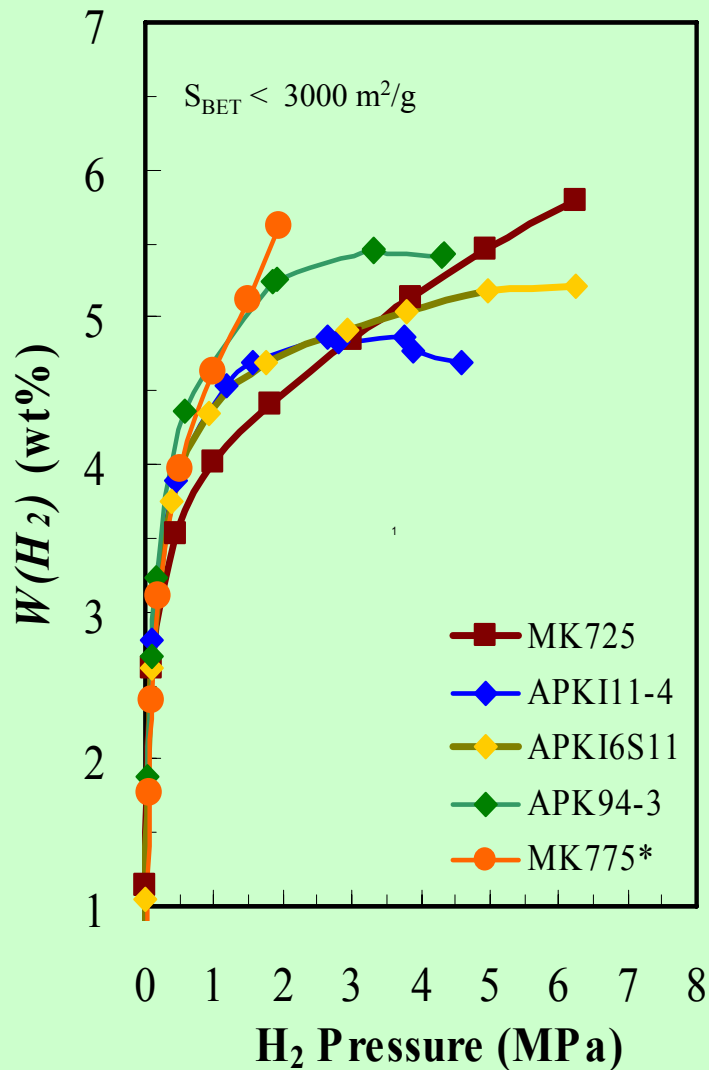
## Correlation of Hydrogen Gravimetric Capacity With Specific Surface Area at 77 K and 1 Bar



- Gravimetric capacity increases as surface area increases at  $\sim 19 \mu\text{g H}_2/(\text{m}_2/\text{g})$  below surface area of  $\sim 1800 \text{ m}^2/\text{g}$ ;
- Gravimetric capacity of  $\sim 3.0 \text{ wt}\%$  is achieved with surface area of  $\geq 1800 \text{ m}^2/\text{g}$  at 77 K and 1 bar.



The influence of pore size on hydrogen gravimetric and volumetric capacity (77 K, 1 bar). Small pores increase hydrogen uptake density.



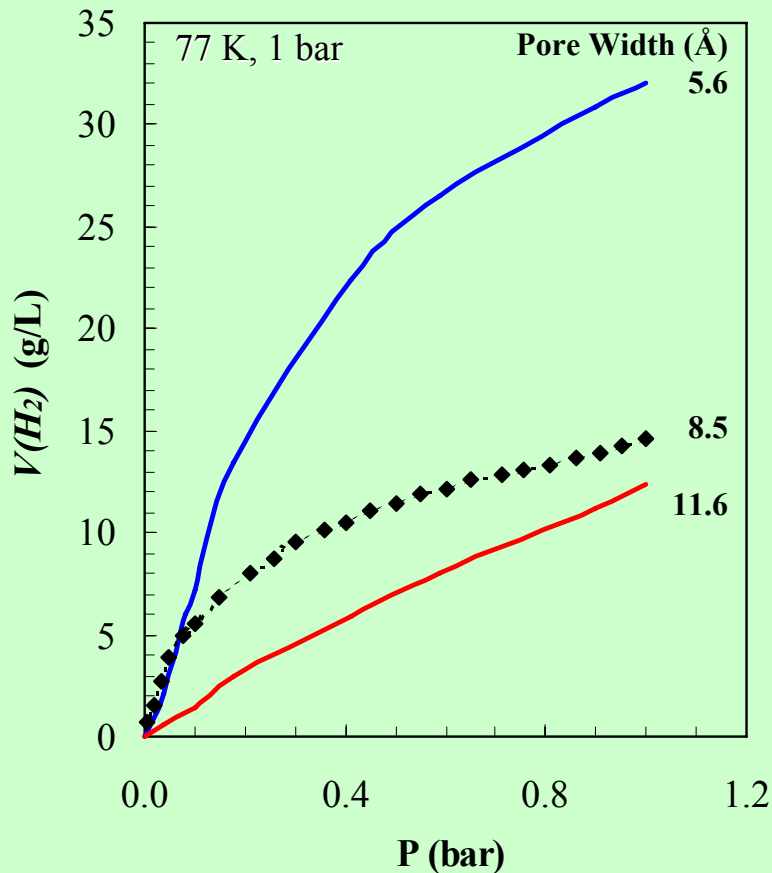
### Excessive Hydrogen Uptake of Polymer Carbons at 77 K and High Pressure

- The gravimetric storage capacity recorded up to  $\sim 6.7 \text{ wt}\%$ ;
- Carbon samples synthesized in this laboratory were sent to multiple institutions for high pressure hydrogen uptake. The data show measurement conducted by: *Gas Technology Institute, Inc., Université du Québec à Trois-Rivières and Oak Ridge National Laboratory.*

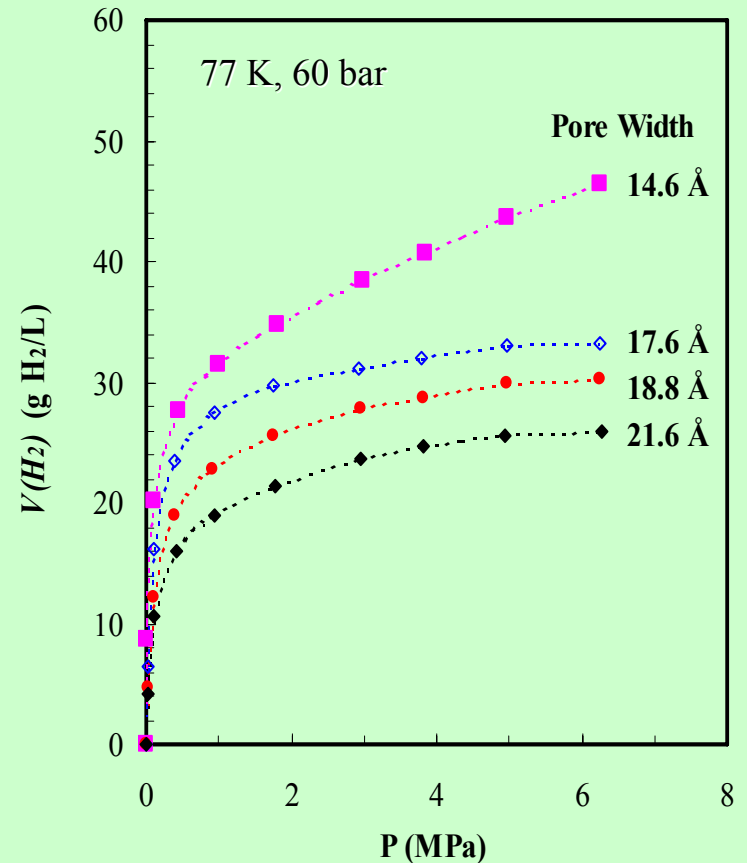
\* MK775 measured up to 2 MPa due to instrument limitation.



# Impact of Pore Size on Hydrogen Volumetric Density

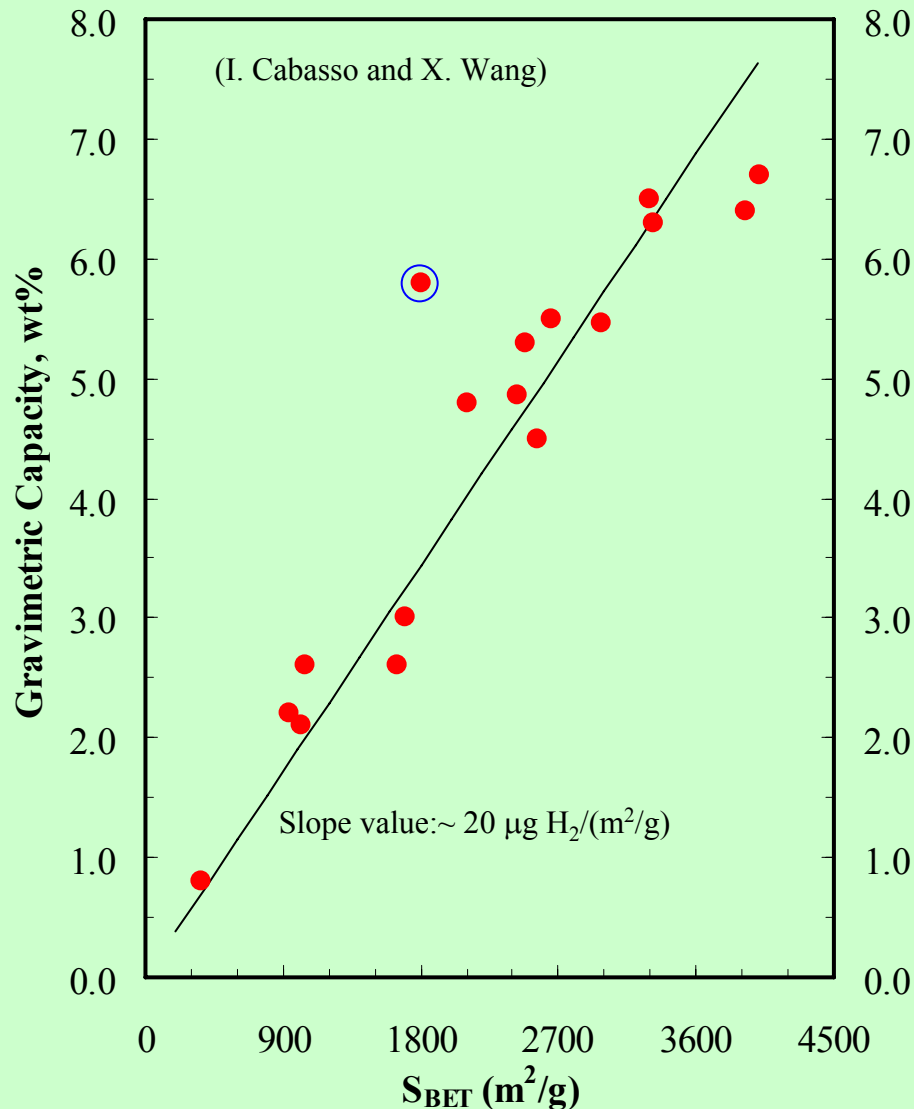


At 77 K and 1 bar, experimental hydrogen adsorption of polymer carbon with a pore width of  $\sim 8.5$  Å falls between the computer simulated data for carbons having a pore width of 5.6 and 11.6 Å [Kowalczyk, et al., *Langmuir*, 2006, 22, 1970].



At 77 K and 60 bar, experimental data shows that decreasing the pore size increases H<sub>2</sub> volumetric density.

## Dependence of Maximum Hydrogen Uptake at 77 K on BET Surface Area



- Maximum hydrogen uptake increases linearly with surface area, at a rate of  $\sim 20 \mu\text{g H}_2/(\text{m}^2/\text{g})$ , which indicates  $\sim 6 \text{ H}_2$  molecules occupy 20 graphene hexagon units. [Hirscher, et al., *Carbon* **2005**, 43, 2209]
- A gravimetric capacity of up to 6.7 wt% has been achieved on a high surface area carbon ( $S_{\text{BET}} \sim 4000 \text{ m}^2/\text{g}$ , pore vol  $\sim 2.30 \text{ mL/g}$ ).
- The circled sample has a microporosity of  $\sim 96\%$  with an average pore width of  $\sim 14.2 \text{ \AA}$ , and exhibits a volumetric capacity of up to 45 g  $\text{H}_2/\text{L}$ .

# Progress Project Summary

## Hydrogen Storage Capacity of Polymer-Derived Carbon Nanostructures

Sample	Polymer	Porous Texture				H <sub>2</sub> Storage, 77 K	
		$S_{BET}^a$ (m <sup>2</sup> /g)	Pore Vol. (mL/g) <sup>b</sup>	Microporosity (%)	$d_{DR}^c$ (Å)	Gravimetric (wt%)	Volumetric <sup>d</sup> (g/L)
MK725*	PEEK	1800	0.87 (0.84)	96.6	14.6	5.8	(45)
APKI11-4	PEEK/PEI	2110	1.03 (0.98)	95.1	16.1	4.8	(33)
APKI6S11	PEEK/PEI	2480	1.20 (1.14)	95.0	17.6	5.3	(33)
APK94-3	PEEK	2650	1.54 (1.32)	85.7	20.2	5.5	(29)
MK775	PEEK	2680	1.15 (1.10)	95.1	17.2	5.6	(37)

Sample	Polymer	Porous Texture				H <sub>2</sub> Storage, 77 K	
		$S_{BET}^a$ (m <sup>2</sup> /g)	Pore Vol. (mL/g) <sup>b</sup>	Microporosity (%)	$d_{DR}^c$ (Å)	Gravimetric (wt%)	Volumetric <sup>d</sup> (g/L)
APKI6S7	PEEK/PEI	3320	1.67 (1.49)	89.2	19.1	6.3	(31)
APKI6SN3	PEEK/PEI	3300	1.85 (1.47)	79.5	18.8	6.5	(30)
APO60S-R10	PPO	3920	2.20 (1.72)	78.1	22.1	6.4	(25)
APKI6SN5	PEEK/PEI	4020	2.30 (1.75)	76.1	21.6	6.7	(26)

# Summary

- **Demonstrated synthesis of carbons with high surface area (up to 4000 m<sup>2</sup>/g) and low average pore width (down to 8.5 Å);**
- **Accomplished gravimetric storage capacity of ~ 6.7 wt%, and volumetric capacity of ~ 45 g/L at 77 K, 5 - 6 MPa.**
- Formulated synthetic strategies toward polymer-based nanostructured carbons of controllable porosity and surface area;
- Achieved reproducibility (>98% in terms of surface area and pore volume) in 10-gram scale batch production of high surface area carbon;
- Enabled carbon doping with organometallic compounds that exhibit rigid planar configuration and are rich in electronegative nitrogen atoms,  $[CNH]_n$ , may enable application for RT and moderate pressure H<sub>2</sub> storage system;
- Established correlation of hydrogen storage with surface area, pore size and porosity;
- Demonstrated hydrogen storage capacity of up to ~3.0 wt% at 77 K and 1 bar.

## Planned work for FY08-FY09:

- ➡ Continue to develop, modify, characterize and scale-up produce nanoporous polymer materials and carbons.
- ➡ Continue to develop methods of doping polymer – blend / carbon with metal hydrides (e.g.,  $\text{MgH}_2$  and  $\text{RSiH}_n$ ), organometallic and multicyclic ligand compounds.
- ➡ Increase hydrogen binding energy by surface modification and doping with heterocyclic and heteroaromatic polymers.
- ➡ Characterization of doped activated carbons and hydrogen storage capacity evaluation.
- ➡ Elevated temperature hydrogen adsorption tests of organometallic-doped PEEK carbons.