

Final Report

Project Title: Optimizing the Binding Energy of Hydrogen on Nanostructured Carbon Materials through Structure Control and Chemical Doping

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Recipient: Duke University

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Summary:

The DOE Hydrogen Sorption Center of Excellence (HSCoE) was formed in 2005 to develop materials for hydrogen storage systems to be used in light-duty vehicles. The HSCoE and two related centers of excellence were created as follow-on activities to the DOE Office of Energy Efficiency and Renewable Energy's (EERE's) Hydrogen Storage Grand Challenge Solicitation issued in FY 2003.¹ The Hydrogen Sorption Center of Excellence (HSCoE) focuses on developing high-capacity sorbents with the goal to operate at temperatures and pressures approaching ambient and be efficiently and quickly charged in the tank with minimal energy requirements and penalties to the hydrogen fuel infrastructure. The work was directed at overcoming barriers to achieving DOE system goals and identifying pathways to meet the hydrogen storage system targets. To ensure that the development activities were performed as efficiently as possible, the HSCoE formed complementary, focused development clusters based on the following four sorption-based hydrogen storage mechanisms:

1. Physisorption on high specific surface area and nominally single element materials
2. Enhanced H₂ binding in Substituted/heterogeneous materials
3. Strong and/or multiple H₂ binding from coordinated but electronically unsaturated metal centers
4. Weak Chemisorption/Spillover.

As a member of the team, our group at Duke studied the synthesis of various carbon-based materials, including carbon nanotubes and microporous carbon materials with controlled porosity. We worked closely with other team members to study the effect of pore size on the binding energy of hydrogen to the carbon-based materials. Our initial project focus was on the synthesis and purification of small diameter, single-walled carbon nanotubes (SWNTs) with well-controlled diameters for the study of their hydrogen storage properties as a function of diameters. We developed a chemical vapor deposition method that synthesized gram quantities of carbon nanotubes with average diameter size at less than 1 nm. However, initial tests performed at our collaborator's lab at the National Renewable Energy Laboratory (NREL) did not indicate improved hydrogen sorption properties for the smaller-diameter nanotubes (compared with other types of nanotubes). As work continued, the difficulties in purification, large-scale synthesis, and stability of small diameter SWNTs became a major concern. In 2008, the Department of Energy (DOE) made a no-go decision on future applied R&D investment in pure, undoped, single-walled carbon nanotubes for vehicular hydrogen storage.²

The second phase of the project involved developing a low-cost and scalable approach for the synthesis of microporous carbon materials with well-controlled pore sizes that would be suitable for hydrogen storage. The team studied several approaches, including the use of different zeolites as a template, the use of organic micelle structures as a template, and the slow oxidation of polymer precursors. Among them, the slow activation of Polyether ether ketone (PEEK) under either CO₂ environment or H₂O vapor produced microporous carbon with an average pore size of less than 2 nm. Initial testing at 77K at both NREL and the California Institute of Technology (CalTech) showed that these materials can store ~5.1 wt% hydrogen (excess) at 40 bar and 77K. The main feature to note with this material is that while the excess gravimetric capacities (>5 wt% at 77K) and specific surface areas (>3100 m²/g) are similar to AX-21 and other "super activated" commercial carbon sorbents at the same temperatures and pressures, due to the smaller pore sizes, bulk densities greater than 0.7 g/ml can be achieved, enabling excess volumetric capacities greater than 35 g/L; more than double that of AX-21.

Project Objectives and Achievements:

The objectives of the project, in both Phase I and Phase II were the following:

Phase I:

1. Growth of uniform nanotubes with controlled diameters:

By using identical nanocluster molecules with different sizes as catalysts for nanotube growth, we expect to control the diameter of the produced uniform nanotubes. Milligram to gram quantity uniform nanotubes will be produced to provide to other team members for the testing of their performance as a hydrogen storage media and studying the diameter dependence of the nanotube-hydrogen interaction.

2. Nanotube “cloning”:

We will study the re-growth and “cloning” of nanotubes in close collaboration with the Hydrogen Sorption Center of Excellence (HSCoE) by depositing these cluster molecules on the open ends of existing short nanotubes that were pre-sorted according to their size and helicity. We believe if nanotubes grow from these catalysts, the new nanotubes will adapt the same helicity as the seeding short nanotubes. By starting with nanotubes seeds with known size and helicity, we can precisely control the type of nanotubes produced.

Phase II:

1. Methods for pore size control in microporous carbon materials:

The goal is to synthesize microporous carbon materials with controllable pore size distribution using organic molecules as templates. Different surfactant molecules and different annealing temperature will be used to control the pore size distribution in the materials. Compared with other approaches, such as Carbide-Derived-Carbons (CDC) and Zeolite-templated carbon materials, this approach will offer more flexible control of pore size and doping concentration. It also avoids the use of chlorine and HF.

2. Doping of the porous carbon materials with metal atoms and boron atoms:

Another goal is to develop methods to use simple precursors containing metal atoms and Boron atoms to prepare microporous carbon with controlled doping. This project will demonstrate the change in hydrogen binding energy through doping and do systematic studies on the effect of pore size and doping level to discover the optimum binding energy for hydrogen. This project will also demonstrate that these materials have potential to exceed the 2015 DOE system goal of 5.5 wt% and 0.040 kg H₂/L by volume when embodied in a system¹.

Achievements:

For Phase I of the project, we focused on the synthesis and purification of small diameter carbon nanotubes. The synthesis method of small diameter single walled carbon nanotubes (CNT) was developed and prepared in gram quantity and resulting materials were tested. However, the characterization and performance testing of the materials did not show any enhancement in hydrogen storage. Nevertheless, our research has contributed to the understanding of the

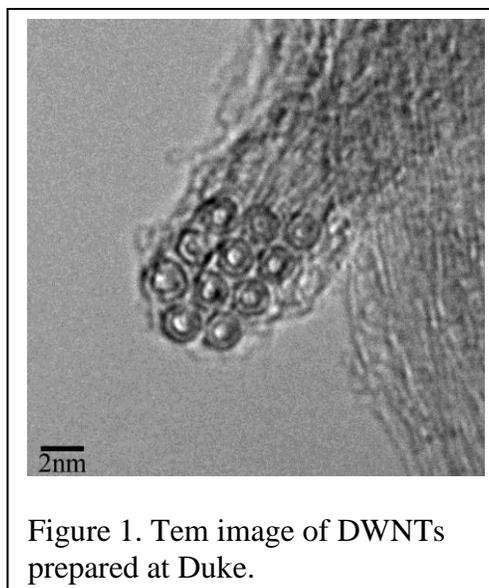
behavior of carbon nanotubes in the area of hydrogen storage. The achievements we had for the Phase I of the project are the following:

1. **Developed understanding on the relation between the carbon feeding rate and the diameter of the prepared nanotubes.** Identified conditions under which small diameter CNTs can be prepared in bulk quantity. As shown in Table 1, the diameter of nanotubes prepared using powdered catalysts containing MgO, Mo and Co alter systematically as a function of the growth temperature:

Growth Temperature	Products
750° C	Single walled carbon nanotubes (SWNTs), less than 1nm in diameter
800° C	Mixture of SWNTs & double walled carbon nanotubes (DWNTs) with 1-1.5nm average diameter
850° C	Mixture of DWNTs & SWNTs with more DWNTs, diameter around 1.5nm
900° C	Mixture of DWNTs and triple walled carbon nanotubes (TWNTs), diameter between 2-3nm
950° C	Mostly DWNTs and TWNTs, diameter between 2-3nm.
1000° C	Mostly CNTs with three and four walls, diameter around 4nm.

Small diameter single walled carbon nanotubes can be prepared as raw samples by reducing the growth temperature to 750 °C. However, due to instability of the small diameter nanotubes against oxidation, nanotubes with smallest diameters (<0.8 nm) disappeared after purification. As a result, the purified samples have average diameters of ~ 1nm. Such small diameter nanotube samples were provided to other center members for the characterization in comparison with other types of nanotubes. Samples were all measured at 77K and 2bar at NREL. The results did not indicate a noticeable increase in the storage capacity.

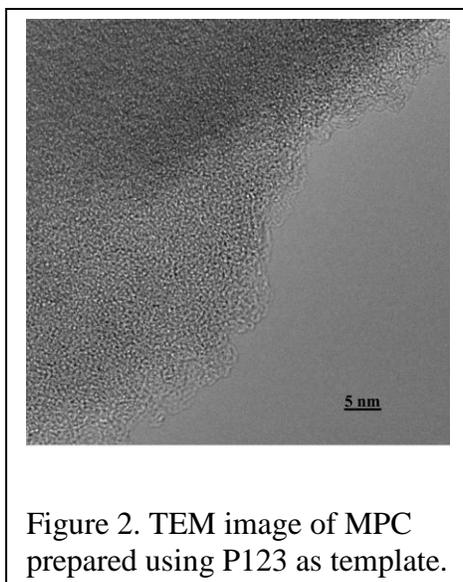
2. **Prepared high purity double walled carbon nanotubes for testing of their hydrogen storage properties.** A publication in 2006 indicated that double walled carbon nanotubes exhibit better hydrogen storage capacity than single walled carbon nanotubes.³ To verify such claims, bulk quantity double walled carbon nanotubes were prepared at Duke (Figure 1) and provided to NREL for measurement. Initial test results did not indicate the improved storage capacity in the double walled carbon nanotubes.



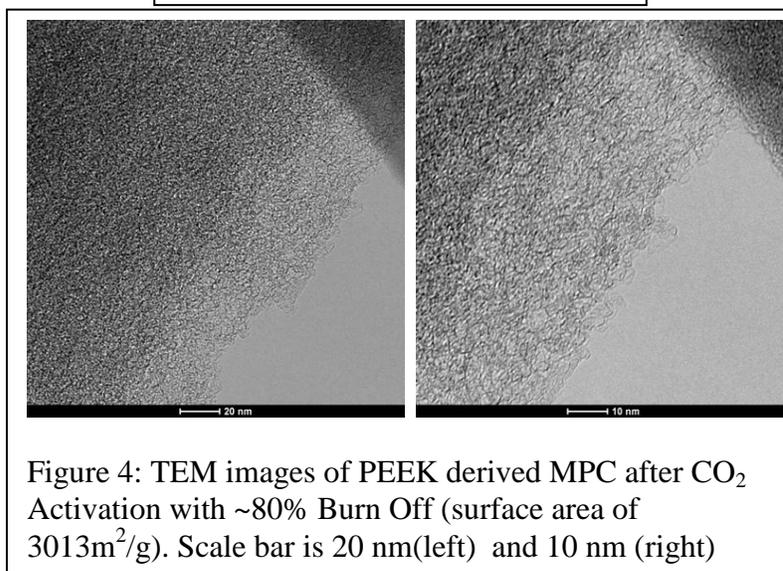
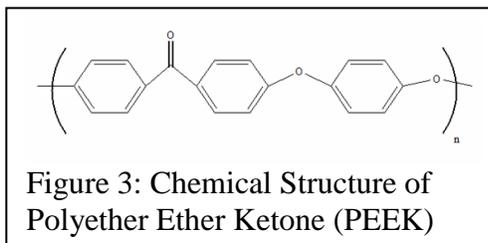
3. **Contributed to the decision of applied R&D down-select decision on pure carbon nanotubes in the area of hydrogen storage for vehicular applications.** The key problem that we have encountered in our research is the high cost of the materials and difficulty in purification. Considering the materials' cost and labor cost involved in the preparation of the small diameter carbon nanotubes, it is not a cost effective way for the storage of hydrogen.

Phase II of the project shifted the focus on the synthesis of microporous carbon materials with controlled pore diameters. We have explored several different methods in obtaining microporous carbon materials, including the use of organic template, inorganic template and direct graphitization/activation without any template using polymer precursor. The achievements in Phase II of the project are listed below:

1. **Developed methods to prepare microporous carbon materials (MPC) using organic surfactant as a template.** Microporous carbon materials with controllable pore sizes were made using different surfactants as organic templates (Figure 2). The pore size of the materials can be controlled by choosing different surfactant as template. For example, the average pore size of the produced MPC is around 1.3 nm for samples made using Pluronic® P123 surfactant from BASF as template and 1.2 nm for samples prepared using Pluronic® P103 surfactant as template. The advantages of the materials are the flexibility and large number of surfactants that can be chosen from. The disadvantage of the approach is the relative low surface area compared to the direct graphitization/activation from polymeric precursors. Therefore, the focus of the Phase II project was shifted to the later approach. However, the use of organic template for the preparation of MPC materials is still a very interesting area of research. If possible, more research needs to be done in the controlling of the pore size and the increase of surface area of the materials.



2. **The use of inorganic template for the preparation of microporous carbon materials.** We have developed the use of zeolite as hard template for the synthesis of MPC materials. However, the scalability of the approach is a challenge and the removal of the inorganic template has been shown to be difficult. The approach was discontinued at Duke.



3. **Development of a direct graphitization/activation method for the synthesis of MPC materials from polymer precursors.** This approach became the main focus of the research project at Duke in Phase II. The method, based on the graphitization and slow activation of Polyether Ether Ketone (PEEK) (Figure 3) under either a CO₂ environment or H₂O vapor, produced microporous carbon with an average pore size <2 nm (see Figure 4). The materials have shown many exciting properties and demonstrated superior properties in hydrogen storage compared to other carbon based materials. The achievements that we have achieved using this approach are:
- a. Obtained microporous carbon (pore diameter <2 nm) from PEEK activation; this is important because porous carbons with a high degree of microporosity have been proposed to be best for hydrogen storage
 - b. Obtained a series of samples with high surface area (>3000m²/g) and high microporosity;
 - c. Observed higher hydrogen storage capacity (>3 wt.% excess) at 77K and 2 bar, and >5 wt% at 77K and 40 bar;
 - d. H₂-NMR characterization confirmed the higher hydrogen storage capacity is from the high microporosity, supporting previous claims that microporous carbons are best for hydrogen storage; the measurement at 10 MPa showed >6% storage at 120K.
 - e. Samples showed higher binding energy (8.1 kJ/mol) to hydrogen molecules.
 - f. Achieved bulk densities greater than 0.7 g/ml, enabling excess volumetric capacities greater than 35 g/L; more than double that of AX-21.

Project Activities:

Phase I: Controlled synthesis of small diameter single walled carbon nanotubes:

1. Controlling the diameter of carbon nanotubes by controlling the carbon feeding rate in a reaction chamber

We have setup a CVD system that allows us to precisely control gas composition and humidity in the CVD growth chamber. Carbon feeding rate (CFR) was found to contribute to the diameter distribution of SWNT synthesized. In addition, we also found that humidity is another important factor, though unexpected, that can tune the SWNT diameter distribution.

Ethane was used as carbon feeding source because it allows a wide controllable carbon feeding rate range. The catalyst used was ferric nitrate dissolved in isopropyl alcohol. Wafers for growth were immersed in that solution for 10 seconds and blow-dried afterward. This method would generate nanoparticles on the surface with a wide diameter distribution, which allowed growth of SWNT with certain diameter range at different carbon feeding rates. Diameter data are based on AFM topographic measurements.

Figure 5 shows diameter distribution of SWNTs produced with different ethane concentration, which corresponds to different carbon feeding rates. At high CFR, diameter of SWNTs increased, and a lot of large diameter carbon nanotubes (possibly MWNTs) appear. We believe that the reason is because higher CFR allowed larger catalyst particles to be activated for SWNT growth while at low CFR level, only small diameter SWNTs growth was allowed for limited carbon feeding.

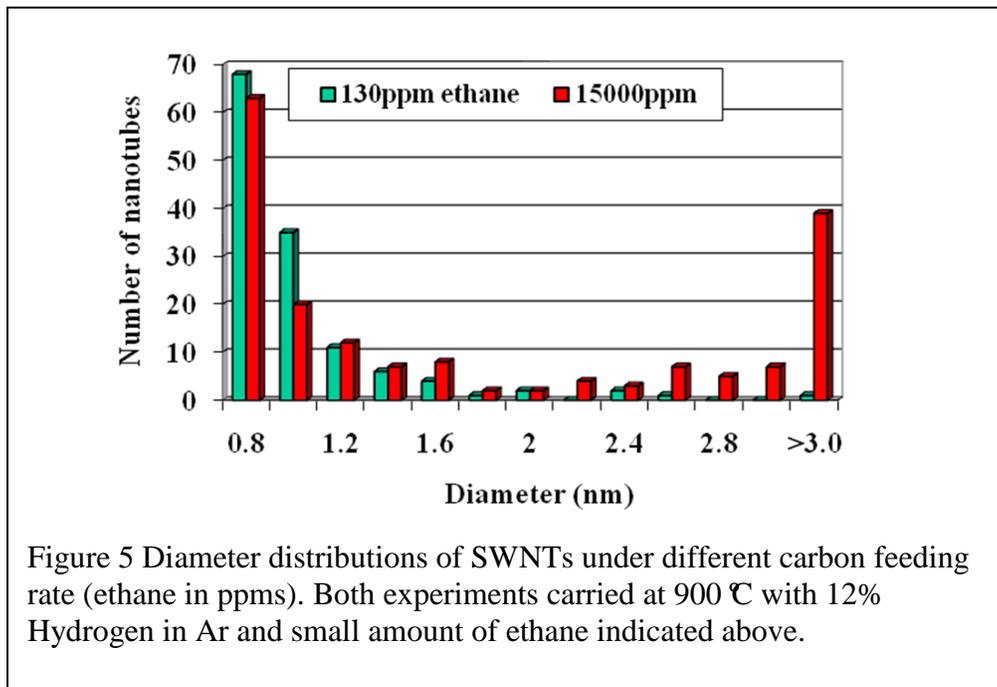


Figure 6 shows humidity effect on diameter distribution. At similar CFR, water played a significant role in controlling the diameter distribution of SWNTs. When water was added, the

peak at small diameter SWNTs levels off, which indicated that water eliminated small diameter growth. It is known that small diameter SWNTs are thermodynamically more active. Therefore, we believe water, which is a weak oxidizer, could quench the formation of small diameter SWNTs or remove them even before they start growing.

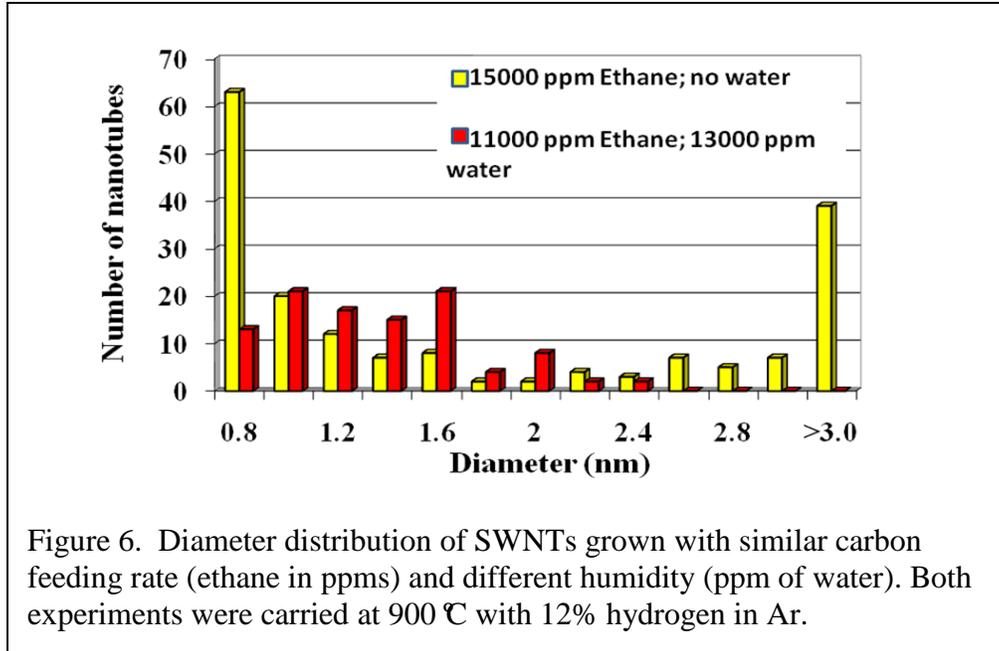
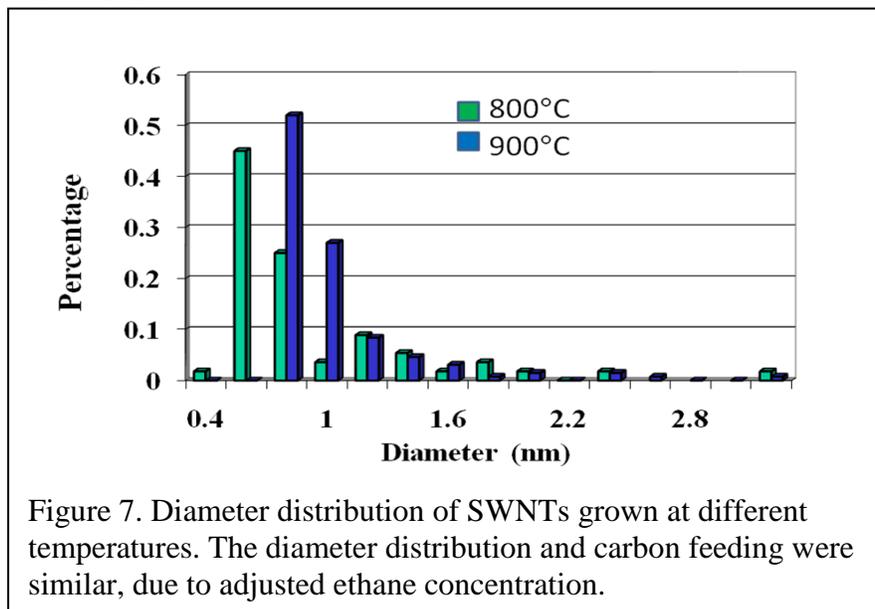


Figure 7 shows the temperature dependence of diameter distribution. At different temperatures, different carbon concentration was used to achieve similar CFR, thus similar SWNT diameter distribution. In conclusion, CFR was found to be able to tune SWNT diameter for CVD growth.⁴ Moreover, controlling of dryness in the growth chamber was found to be important in production of small diameter SWNTs.



2. Chemical Vapor Deposition of Small Diameter Single-Walled Carbon Nanotubes Using Cobalt Diblock Copolymer as Catalysts

Growth of SWNTs in small diameter and narrow distribution such as less than 1 nm is highly desired in order to control the geometrical arrangement. In the CVD growth of SWNTs, the diameter of SWNTs is determined by the size of the catalyst. We have explored the growth of small diameter SWNTs using cobalt diblock copolymer as catalyst which results in small diameter nanoparticles.

After removing the organic component of the cobalt diblock copolymer catalysts with oxygen plasma, Cobalt oxide nanoparticles were generated on the surface. Figure 8a shows the AFM image of Cobalt oxides nanoparticles on the surface. The nanoparticles were distributed on the surface with high density. The average diameter of these particles is about 1.5nm. No aggregation was observed on the surface.

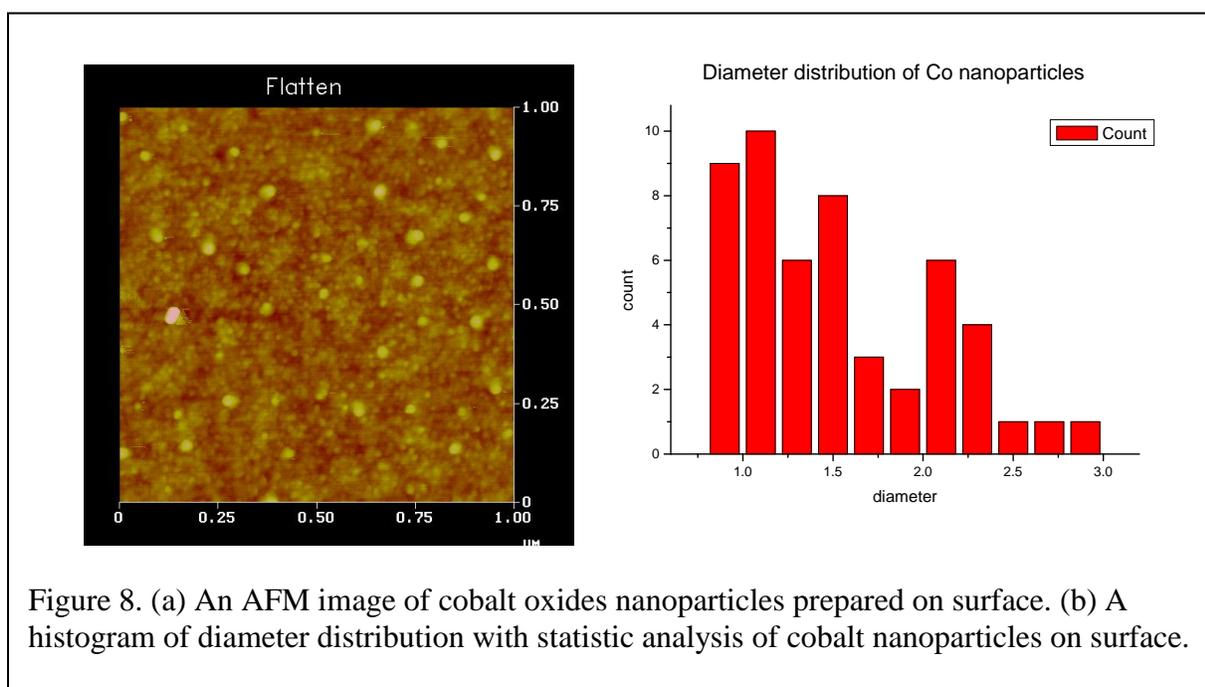


Figure 9 shows a SWNT thin film with high density on the surface. The SWNTs are overlapped and form a dense network. The growth condition is 60 sccm of H₂ mixed with 800 sccm of CH₄ grown at 900 °C. The high density is probably due to the high efficiency of these kinds of catalysts for SWNTs CVD growth.

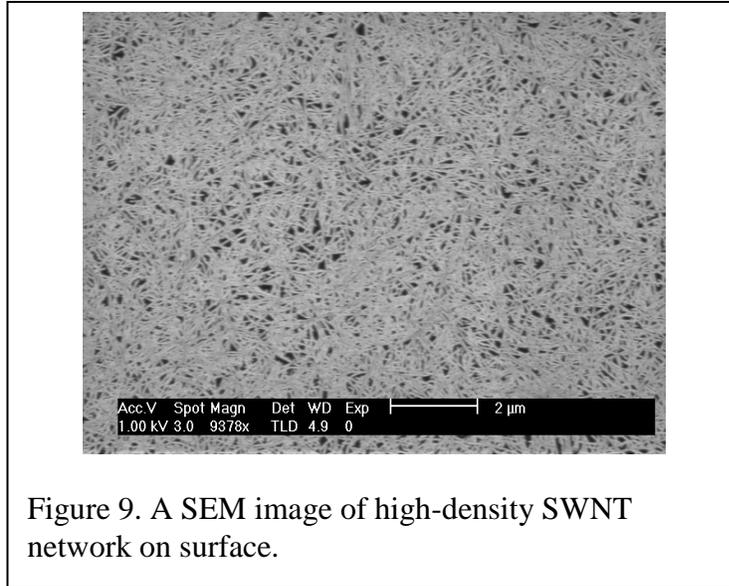


Figure 9. A SEM image of high-density SWNT network on surface.

The diameter of the formed SWNTs is smaller than 1nm and has a narrow distribution range. Figure 10 shows an AFM image of SWNTs on the surface. Surface is clean and free of amorphous carbon probably because of the pure methane growth condition. The average diameter of SWNT is about 0.6nm. The small diameter and narrow distribution results are highly possible due to the uniform size of the catalysts which confine the diameter of SWNTs.

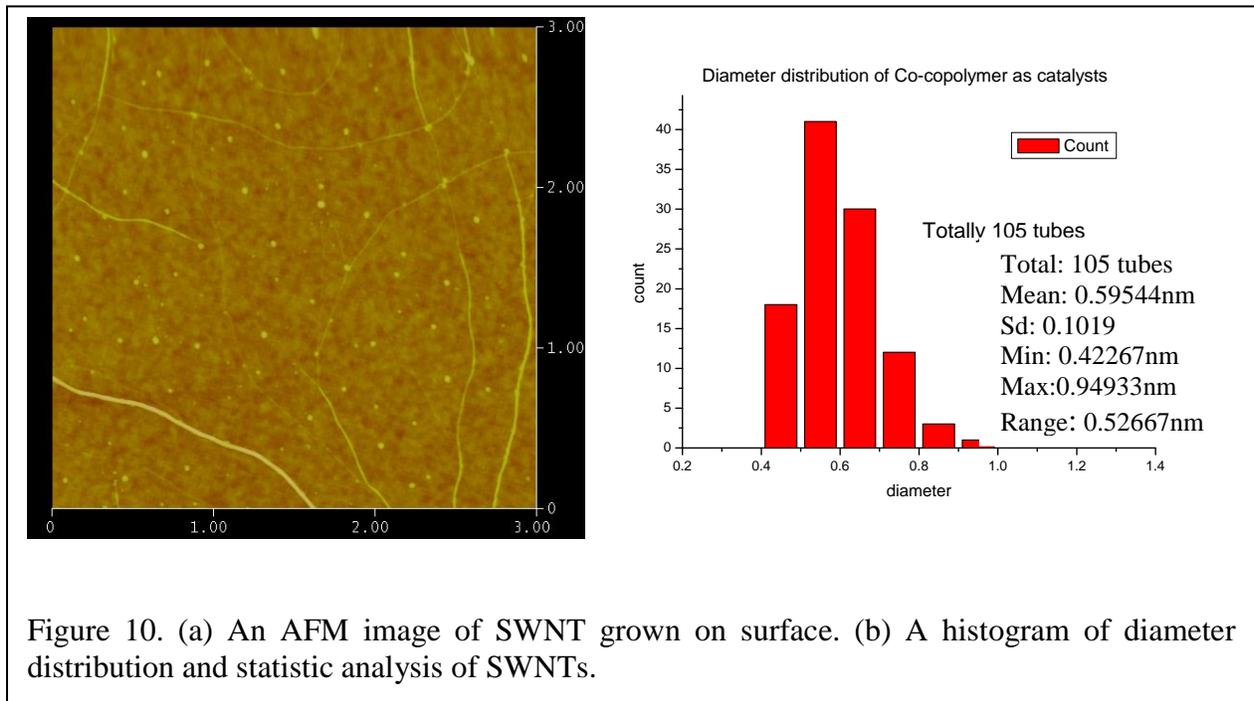


Figure 10. (a) An AFM image of SWNT grown on surface. (b) A histogram of diameter distribution and statistic analysis of SWNTs.

The above results show that Cobalt diblock copolymer is an effective catalyst for SWNT CVD growth. Thus, it is a good choice for diameter control. However, further investigations are

needed to elucidate the growth mechanism. The result provides some guidance for bulk synthesis of SWNTs in gram scale.

3. Gram scale synthesis of small diameter of SWNTs:

In an effort to scale up the production of small diameter SWNTs, we have developed an understanding of the relation between the carbon feeding rate and the diameter of the prepared nanotubes. Using the understanding, we have identified conditions under which small diameter CNTs can be prepared in bulk quantity. As shown in Table 1, the diameter of nanotubes prepared using powdered catalysts containing MgO, Mo and Co alter systematically as a function of the growth temperature:

Table 1: Relation between the Growth Temperature and the Composition of the Products	
Growth Temperature	Products
750 °C	Single walled carbon nanotubes (SWNTs), less than 1nm in diameter
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850 °C	Mixture of DWNTs & SWNTs with more DWNTs, diameter around 1.5nm
900 °C	Mixture of DWNTs and triple walled carbon nanotubes (TWNTs), diameter between 2-3nm
950 °C	Mostly DWNTs and TWNTs, diameter between 2-3nm.
1000 °C	Mostly CNTs with three and four walls, diameter around 4nm.

Small diameter single walled carbon nanotubes can be prepared by reducing the growth temperature to 750 °C using a catalyst containing Co, Mo supported on MgO. The materials were purified by low temperature air burning to remove amorphous carbon in the raw materials and washed with 1m HCl to remove catalyst and support (See Figure 11). Such small diameter nanotube samples were provided to other members within the DOE Sorption Center of Excellence for the characterization of their hydrogen storage properties and comparison with other types of nanotubes. Samples were all measured at 77K and 2bar at NREL (See Table 2). The results did not indicate any noticeable increase in the storage capacity as a function of the smaller diameter. However, more measurements are needed to identify whether the binding energy of hydrogen molecules on such materials is different from nanotubes with larger diameters.

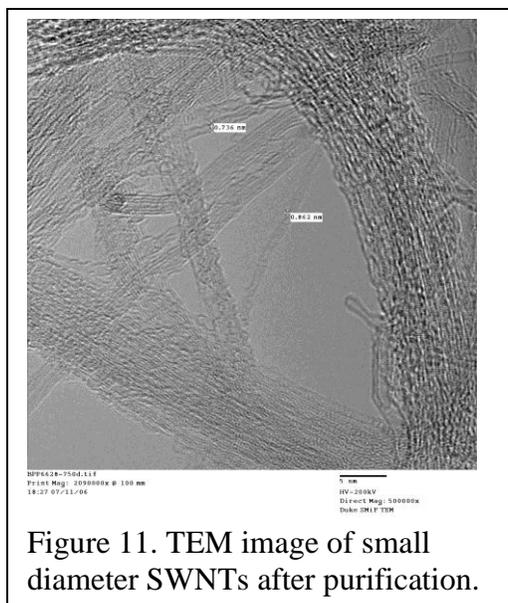
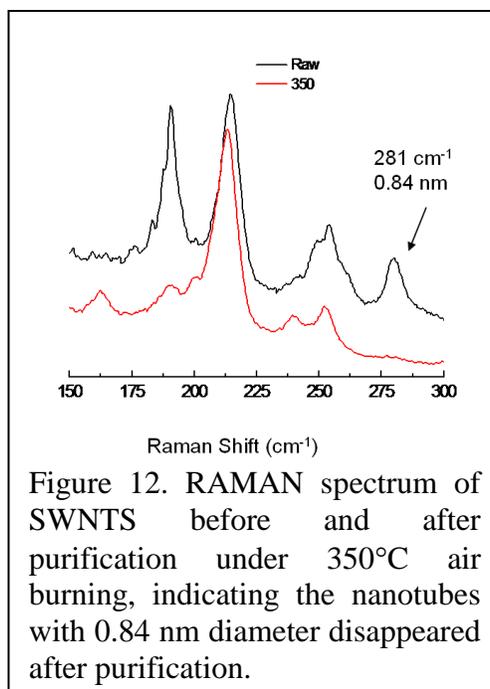


Figure 11. TEM image of small diameter SWNTs after purification.

Measurement	0.9 nm SWNT	1-2 nm SWNT/DWNT	0.9 nm SWNT + 2 nm Pd	1-2 nm DWNT	Small d Commercial SWNT	Typical NREL SWNT
Sieverts RT & 2 bar as received	0.007 wt%	0.011 wt%	0.36 wt%		0.04 wt%	
Sieverts 77 K & 2 bar as received	0.39 wt%	0.54 wt%	0.58 wt%	0.04 wt%	1.13 wt%	
BET SA as received	350 m ² /g	420 m ² /g	269 m ² /g	42 m ² /g		
Modified Chahine Criterion (wt% per 500 m ² /gm)	0.56	0.64	1.08	0.48		
TPD: 500 torr dose at RT cooled to 77K as received			0.39 wt% total ~0.24 wt% Pd, ~0.15 wt% Chemi.			
Sieverts 77 K & 2 bar after 800 °C degas				0.11 wt%	1.43 wt%	
BET SA after 800 °C degas				82 m ² /g	880 m ² /g	
Sieverts 77 K & 2 bar after 800 °C					1.61 wt%	
BET SA after 800 °C CO2				75 m ² /g	1074 m ² /g	
Sieverts 77 K & 2 bar after H ₂ SO ₄ reflux, CO ₂ to 700 °C, HCL soak, CO ₂ to 700 °C		0.84 wt%				1.7 wt%
BET after H ₂ SO ₄ reflux, CO ₂ to 700 °C, HCL soak, CO ₂ to 700 °C		630 m ² /g				630 m ² /g
Modified Chahine Criterion (wt% per 500 m ² /gm)		0.67		0.67	0.75	1.35

Table 2. Detailed Characterization of different SWNTs at 77K and 2bar (From NREL)

On the other hand, the characterization of the raw and purified materials using RAMAN spectroscopy has disclosed interesting insights. As shown in Figure 12, the RAMAN peaks corresponding to the nanotubes with the smallest diameters disappeared after purification. This is not totally surprising since the small diameter carbon nanotubes are more reactive to oxygen due to the higher strain in their structures. However, the results indicated that obtaining pure small diameter SWNTs is a major challenge since the differences in their chemical reactivity between the small diameter carbon nanotubes and amorphous carbon are small.



Even though purified nanotubes with average diameter < 1nm can be obtained by lower temperature (300 °C) oxidation. The purity of the samples is not high. Additionally, nanotubes with diameters less than 8 nm still disappeared after purification. There is a need for other purification methods to remove impurities, mostly amorphous carbon, without the use of an oxidizing environment. A possible solution is the use of an ultra centrifuge to remove impurities from the nanotubes. However, the high cost related to such purification methods makes the production of large amounts of small diameter carbon nanotubes difficult. With this information and other related knowledge obtained by members of the CoE, the use of pure SWNTs for vehicular hydrogen storage received a no-go decision from DOE and thus these applied R&D efforts were discontinued in Phase II of the project. As a result of the decision, the focus of the project at Duke shifted from the synthesis of SWNTs with small diameter to the synthesis of small pore size microporous carbon materials (MPC). As will be discussed in the next section, we have explored several different methods for the synthesis of microporous carbon materials and developed methods for the large scale production of MPCs with low cost and high hydrogen uptake.

Phase II: Controlled synthesis of microporous carbon materials and optimizing the binding energy of hydrogen

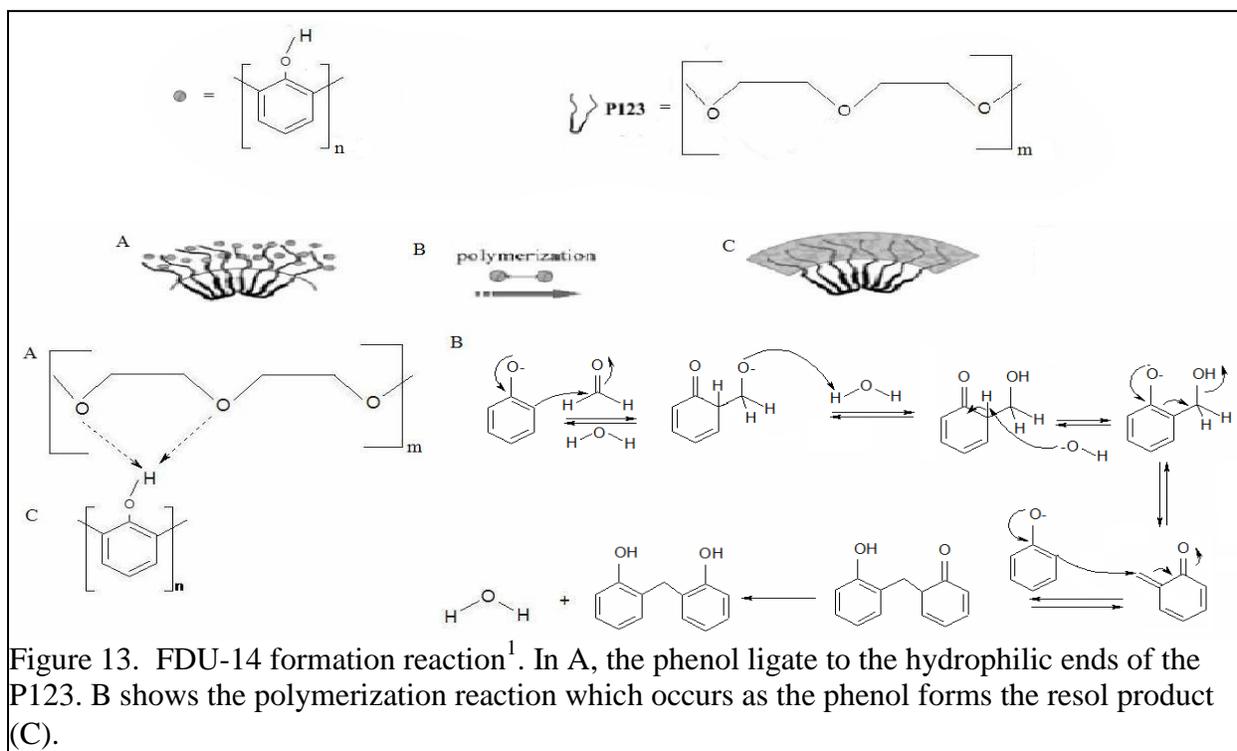
1. Synthesis of MPCs using organic templates:

The first approach we explored was the synthesis of MPC materials using inorganic templates. Furfuryl alcohol (FA) was encapsulated in Faujasite Zeolite Y (FAU) and heated at 700°C for 3 hrs. The main problem that we have encountered is the difficulty in removing the residual zeolite. The zeolite impurities can be easily seen under TEM. In order to solve this problem, we explored the use of organic template for the synthesis of MPC materials. The main approach was the following:

- Using various surfactant molecules to form micelles in a solution. Different surfactants will form micelles with different sizes;

- Introduce a polymer precursor into the solution that will interact with the outer surface of the micelles;
- Trigger the polymerization reaction to form a strong framework of polymers using micelles as templates;
- Thermally remove the surfactants;
- Graphitize the polymer at high temperature to form desired materials.

Several publications suggested that mesoporous carbons with scalable pore sizes and high surface area can be made utilizing triblock copolymer P123 as a template.^{5,6} This idea and the mechanism of formation for this new mesoporous carbon (FDU-14) are illustrated in Figure 13. Notice that the micelle behavior of the P123 is the key to using this organic template. The phenol/ formaldehyde polymer resin, or resol, is associated with the hydrophilic end of the P123. Therefore, the size of the micelles determines the pore size of the mesoporous carbon product. Removing this template requires only heating at 350°C for 2 hrs under He or N₂ flow. This is an easy and cheap removal method which produces a large yield. Indeed it doesn't suffer from the contamination, the danger and the lower yields associated with typical acid washes used in inorganic template removal steps.



The formation of MPC using the organic templates relies on the hydrogen bonding of resorcinol to the structure forming surfactants, such as P-123 and P-103 from BASF. The main difference between these two surfactants is their length. These triblock copolymers are comprised of poly(propyleneoxide) (PO) capped on either end with poly(ethyleneoxide) (EO). However, while their lengths are indeed different, the weight percent of EO remains the same. Thus, the length differences are related primarily to the PO content. Being that this section is responsible for pore formation (Figure 14), differing lengths result in different sized pores. Thus MPC's with average

micropore diameters of 1.18nm and 2nm have been demonstrated by utilizing P103 and P123 respectively (Figure 15).

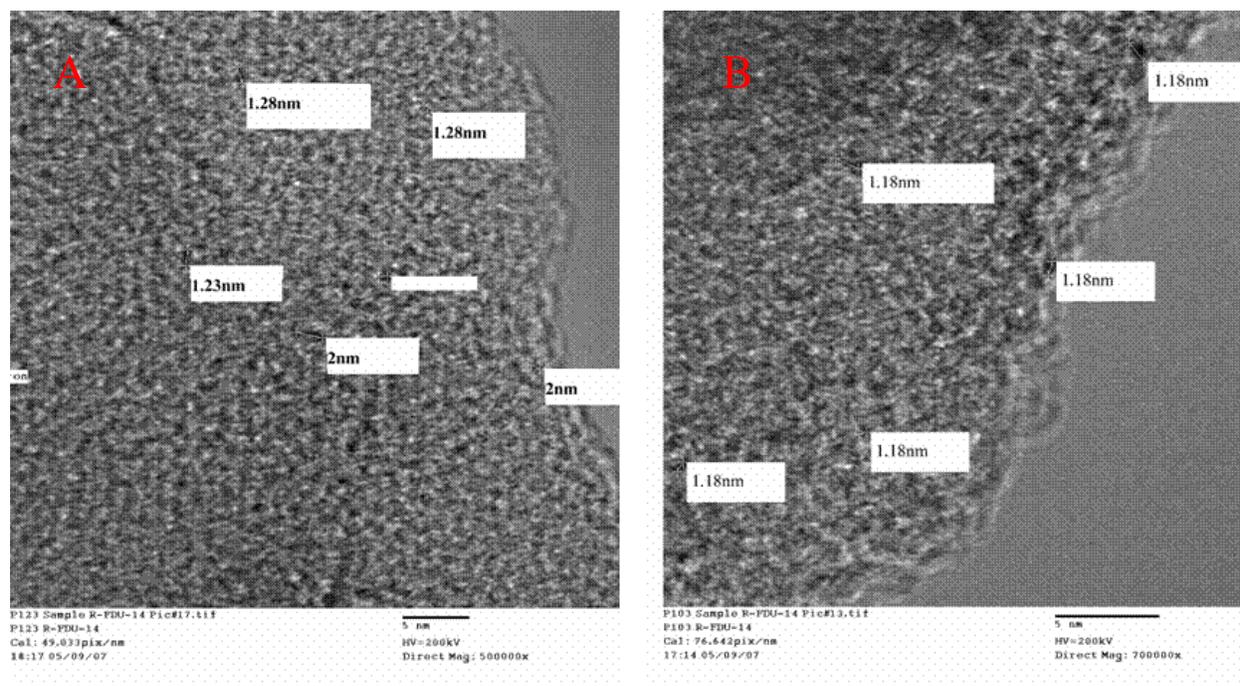
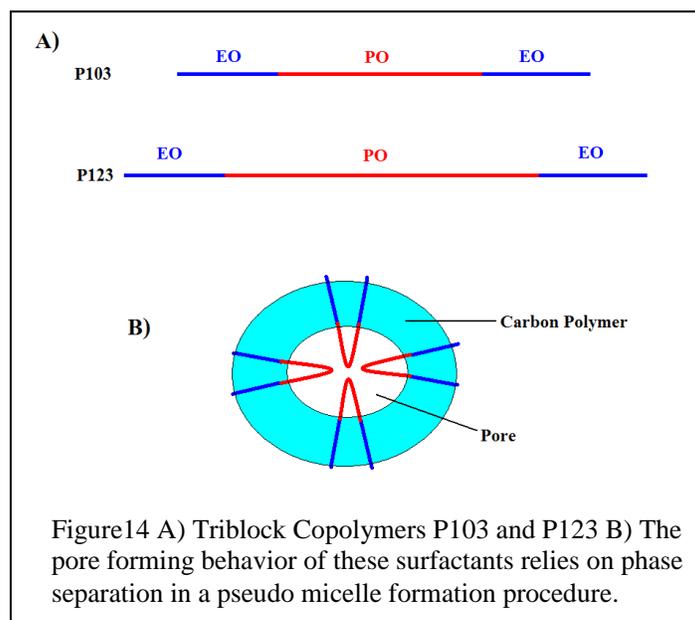


Figure 15 A) MPC made from P123 with pore diameter of ~2nm. B) MPC from P103 with pore diameter of ~1.18nm

The scalability of organic template porous carbon materials has been demonstrated and confirmed by TEM studies. Pores with even smaller pore diameters, 0.6-0.8nm were seen when using the organic template P84 and the resol polymer. However, BET and H₂ analysis indicate

that the achieved material has low surface area ($<250 \text{ m}^2/\text{g}$) and pores inaccessible to H_2 . These conclusions led us to begin investigating various activation methods using a variety of polymers.

2. Synthesis of MPCs from direct graphitization and activation of polymer precursors under mild oxidizing environment:

The methods for graphitization and activation were developed using a published procedure as reference.^{7,8} Typically, five grams of PEEK was placed in an alumina combustion boat from Fisher Scientific, which was then placed inside the one inch quartz reaction tube. UHP Argon gas (Ar) was flowed through the tube at about 700 sccm as the temperature was slowly raised ($10^\circ\text{C}/\text{min}$) from room temperature (25°C) to 900°C and maintained there for 30 min. After this carbonization step, Ar flow was stopped and CO_2 was introduced at 100 sccm for the pre-determined reaction time. After the reaction was complete, Ar was re-introduced and the CO_2 stopped as the reaction tube was allowed to cool to room temperature. After collection, the “Burn Off” (BO) was calculated assuming that the carbonization yield was 51% Cansado. The burn offs were then reported relative to the remaining sample after carbonization. After the BO was calculated, the samples were stored under vacuum desiccation until further analysis. These samples were named PEEK- CO_2 -9-BO. Here, the CO_2 and number nine respectively refer to the gas and temperature (divided by 100) used in the reaction.

In the process for the activation using water vapor (steam), the amount of PEEK and steps taken to carbonize the steam treated samples was the same as for those treated with CO_2 . After carbonization, Ar was allowed to flow at 700 sccm through a 16 oz. bubbler filled with nanopure water (NP H_2O) at room temperature. After being allowed to react for the predetermined reaction time, the pure Ar was re-introduced to the reaction tube as it cooled to room temperature. The BO was calculated the same way as with the CO_2 treated samples and stored under vacuum desiccation. These samples were named PEEK-ST-9-BO. Here, the ST and number nine respectively refer to the gas and temperature (divided by 100) used in the reaction.

Samples were analyzed with a 5 pt. BET analysis using a Micrometrics Gemini 2360 Instrument (Material Synergy). H_2 -NMR was done using a basic free induction decay pulse sequence in a 4.7 T superconducting magnet at pressures ranging from 100 Pa to 10 MPa, at both room temperature (RT, $\sim 290\text{K}$) and 100K (UNC-CH). H_2 sorption measurements taken by our partners at the NREL were done on the following instruments: uptake measurements over 2 bar were made on a Hy-Energy PCTPro-2000, uptake measurements at 2 bar were made on a Sieverts device specially built by our partners at NREL, and BET and pore volume measurements were made on a Quantachrome Autosorb-1. Additional H_2 sorption isotherms were measured at CalTech on a custom Sieverts apparatus. All samples were degassed at 300°C before sorption measurements were conducted. Also, H_2 sorption was assumed to occur instantaneously in these studies. Transmission Electron Microscopy (TEM) images were taken on a FEI Tecnai G²Twin Microscope with an acceleration voltage of 200 kV. Density Functional Theory was used to calculate cumulative pore volumes and diameter distributions.

After thermally treating PEEK under different environments, a blackened and highly porous powder product was formed. TEM and N_2 sorption isotherm analysis shows that these porous products have a relatively narrow distribution of small pores at low percent burn off (BO), while

higher BO products have a slightly broader diameter range. It is generally thought that steam provides a gentler oxidation environment than CO₂. Thus, in this study, steam was used to limit pore diameter widening and therefore investigate the relative importance of the diameter distribution and pore volume to H₂ storage in microporous carbons. Accordingly, characterization of the pore diameter distributions as well as pore volume distributions was integral. Perhaps most importantly, an understanding of the evolutions of each was paramount to appropriately categorize these methods. Such an understanding is necessary for the successful application of these methods and their tailored porous carbon products, especially to H₂ storage aims.

One of the most important factors for H₂ storage by porous materials is surface area. In general at 77K, graphitic slit pore materials typically have excess adsorption capacities of ~1 wt% for every 500 m²/g surface area.⁹ As such, achieving a large surface area is extremely important. Here, we have demonstrated that both CO₂ and steam (ST) can be utilized to produce porous carbons with very large surface areas, in both cases reaching ~3000 m²/g or more. It is critical to note that the samples consist almost entirely of pure carbon, as determined by X-Ray Photoelectron Spectrometry (XPS). XPS data indicated that the surface chemistries of the pores were largely graphitic. Therefore, direct comparison of these CO₂ and steam derived products can be utilized not only to compare these products, but also the importance of pore diameter and volume to H₂ sorption.

Plots in Figure 16 show the evolution of the Brunauer-Emmett-Teller (BET) surface area with BO and demonstrates the large surface area ($\sim \geq 3000$ m²/g) achievable using both methods. It is evident that the surface area increases with increasing BO in both cases. This is in line with the proposed pore formation mechanism in which pores are oxidatively etched from the carbonized PEEK structure. However, CO₂ produces a much more regular and linear increase in BET surface area with BO. Steam produced samples appear to suffer from a significant amount of pore collapse. This could be due to differences in the mechanism of oxidation by CO₂ as compared to steam. If steam did conserve the pore diameter distribution better and increase the pore volume with surface area more than CO₂, this could cause structural collapse at certain periods during the extended thermal treatment process. Essentially, the etching would eventually cause the pore walls that separate individual pores to break down. This fact is supported by NMR investigations of steam products. These investigations show that the peaks of H₂ in micro/mesopores become indistinguishable from those of H₂ in large voids at very high BO. This indicates that most of the pores are connected to each other and to the voids, allowing free exchange of H₂. Thus, steam derived samples reaching 3000 m²/g are not ideal for H₂ storage, and therefore were not analyzed beyond surface area measurements in this work. Therefore, CO₂ is better for achieving stable, large surface area products. However, which method produced the

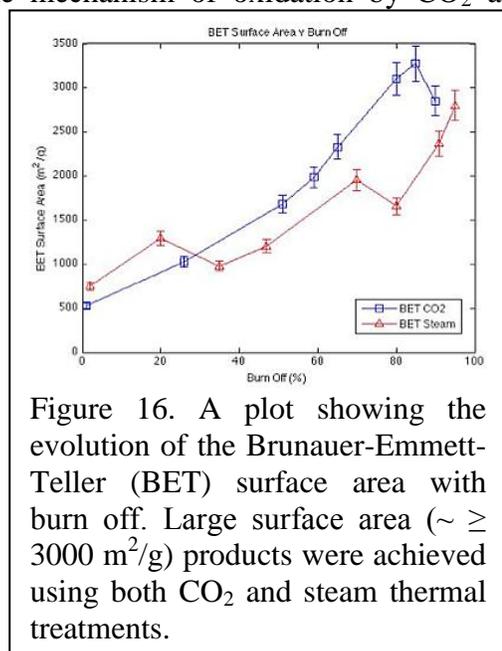


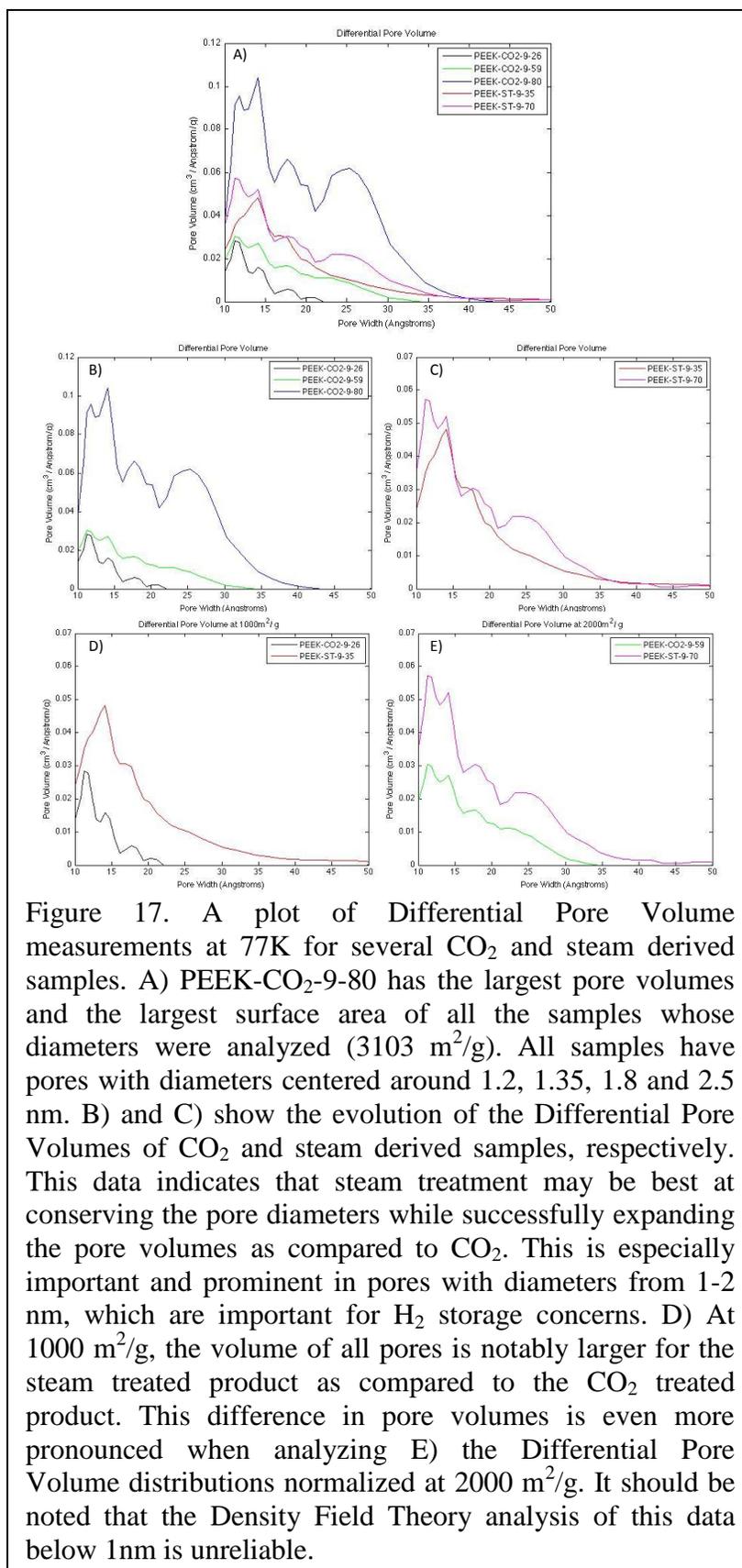
Figure 16. A plot showing the evolution of the Brunauer-Emmett-Teller (BET) surface area with burn off. Large surface area ($\sim \geq 3000$ m²/g) products were achieved using both CO₂ and steam thermal treatments.

samples with the smallest pore diameters and therefore largest pore volumes? Also, how important are these factors to storing H₂?

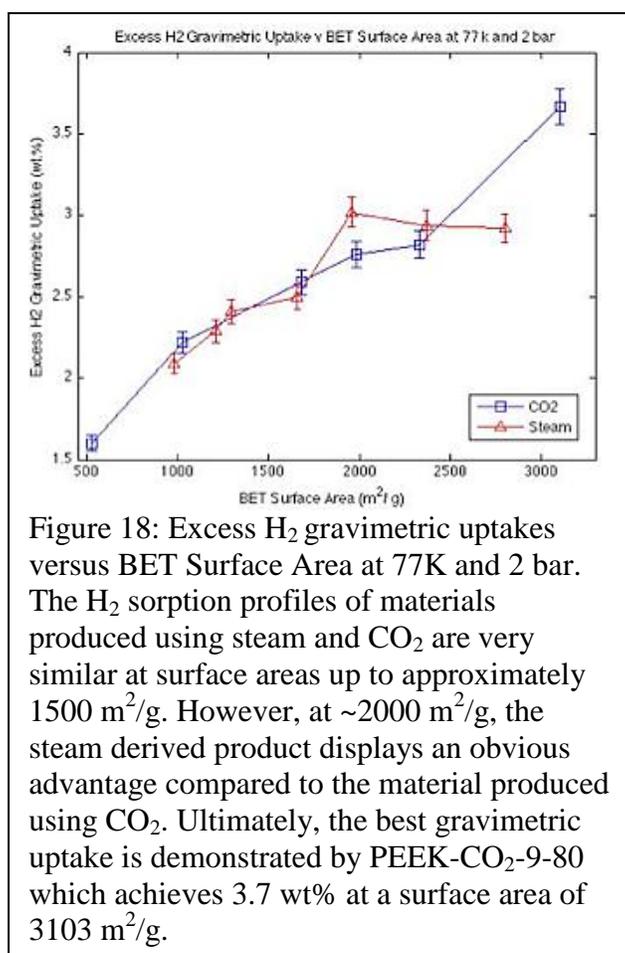
To determine this, Differential Pore Volume measurements were taken to analyze and compare the products of each method. Figure 17A shows that the sample with the largest pore volume is PEEK-CO₂-9-80, which has the largest surface area of all the samples whose diameters were analyzed (3103 m²/g). However, along with the large surface area and pore volumes, the diameter distribution is evidently higher than the other samples with smaller surface areas. This sample has pores of approximately 1.2, 1.35, 1.8 and 2.5 nm with the largest pore volume (0.1 cm³/Å/g) at a diameter of 1.35 nm. However, the pores at 1.8 nm and 2.5 nm also have relatively large pore volumes of approximately 0.06-0.07 cm³/Å/g. While the volume of all pores increases with increasing BO, it is apparent from Figure 17B and C that the larger pores develop “later” than smaller pores. Again, this agrees well with the theory of pore formation, since the etching of the pore walls continues for the entire duration of the treatment, as would pore nucleation. Thus, pores would both widen in diameter and increase in volume as BO progresses.

Figure 17B displays this evolution for samples produced using CO₂. From Figure 17B, it is evident that PEEK-CO₂-9-26 is dominated by pores with diameters <1.5 nm. Also, as BO continues, the volume of pores with diameters ~1.35-2.5 nm increases most noticeably, as demonstrated in PEEK-CO₂-9-59. This represents an increase in BET surface area from ~1000 m²/g to 2000 m²/g respectively between the samples. Increasing the BET surface area further to ~3000 m²/g in PEEK-CO₂-9-80 demonstrates a drastic increase in all pore volumes, with the largest increase in pores with diameters 1.2 and 1.35 nm. Figure 17C shows the same evolution for steam-derived samples. This graph shows that, unlike the CO₂ derived samples, increasing the surface area from ~1000 m²/g to 2000 m²/g in steam treated samples (PEEK-ST-9-35 and PEEK-ST-9-70 respectively) causes the most dramatic pore volume increase in pores with diameter ~1.2 nm. The second most dramatic increase is in pores of diameter ~2.5 nm; however, the pore volume of the 1.2 nm pores increases approximately twice as much as the pore diameter at ~2.5 nm. This seems to indicate that steam treatment may indeed help conserve the pore diameters while successfully expanding the pore volumes, particularly of the crucial pores with diameters around 1 nm. If steam is favorable to CO₂ in this regard, this should be reflected in a comparison of the Differential Pore Volume distributions of steam and CO₂ derived samples normalized to BET surface area.

Figures 17D and E display these comparisons between steam and CO₂ derived samples. Figure 17D displays that, at 1000 m²/g, the volume of all pore diameters is notably larger for the steam treated product as compared to the CO₂ treated product. Also, the pore with the largest volume for this steam sample has a diameter of ~1.35 nm, indicating a predominantly microporous product. The difference in pore volumes is even more pronounced when analyzing the Differential Pore Volume distributions normalized at 2000 m²/g (Figure 17E). Here, it is evident that the pores with diameters of 1.2 and 1.35 nm in steam treated sample have significantly larger volumes than in the CO₂ treated samples. This does support that steam can be utilized to help conserve small pore diameters while increasing the pore volumes of porous carbon products.



The small diameters, large pore volumes and large surface areas of these samples are very impressive among porous carbon materials. Additionally, having both small pores and large surface areas is extremely beneficial for H₂ storage applications. Figure 18 shows the H₂ gravimetric uptake at 77K and 2 bar as it evolves with surface area for samples produced using both steam and CO₂. It should be noted that both methods suffer from a certain degree of pore collapse and pore restructuring during the extended reaction. This is why many of the trends, including H₂ uptake, are not linearly related to surface area. The H₂ sorption profiles of the materials produced using both methods are very similar at surface areas up to approximately 1500 m²/g. However, at ~2000 m²/g, the steam derived product displays an obvious advantage compared to the material produced using CO₂. As was discussed previously, the main difference between these two samples is that the pore volumes of the smaller diameter pores (1.2, 1.35 nm) are notably larger for steam products as compared to CO₂ products.



The larger pore volumes, particularly of these smaller diameter pores, seem to play a noteworthy role in the H₂ storage capabilities of these materials. However, the ability of CO₂ to produce stable samples with large surface areas ultimately overshadows this fact in these samples. Here, these large surface areas (>3000 m²/g) and relatively large pore volumes and small pore diameters combine to produce a sample that has very impressive H₂ sorption capabilities; specifically, PEEK-CO₂-9-80 which achieves 3.7 wt% at 77K and 2 bar. Table 3 compares the materials produced here with several other doped and undoped porous carbon products presently

being investigated within and outside of the DOE Hydrogen Sorption Center of Excellence. It is apparent from this comparison that the materials investigated in this work are among the most impressive and exciting candidates for H₂ storage media. One trend that is particularly interesting is that the gravimetric uptake of these materials outperforms other materials with larger surface areas in many cases. Surface area is a key factor involved in H₂ storage; however in the case of these PEEK derived materials it is obvious that other factors are contributing significantly to their H₂ sorption profiles. For example, PEEK-CO₂-9-80 has a larger H₂ gravimetric uptake compared to AX-21 at the same temperature and pressure.

Material	BET SA (m ² /g)	Excess H ₂ Uptake wt.% §	Volumetric Capacity (g/L)	Cumulative Pore Volume (cm ³ /g)
PEEK-CO ₂ -9-1	524	1.6	11	NA
B/C ¹⁰	780	~1.6 (at 77 K, 1.2 bar)	NA	NA
PEEK-CO ₂ -9-5	700	2.0	14	NA
CMK-1 ¹¹	1788	2.19 (77 K, 1 bar)	NA	NA
PEEK-CO ₂ -9-26	1027	2.2	15	0.63
PEEK-ST-9-47	1207	2.3	16	NA
PEEK-ST-9-20	1294	2.4	17	NA
PEEK-ST-9-70	1956	3.0	18	0.89
AX-21 ¹²	3000	~3.0 (77 K, 2 bar)	NA	NA
PEEK-CO ₂ -9-80	3103	3.7 (~5 at 77 K, 20 bar)	26 (35 at 77 K, 20 bar)	1.7
Corncob ¹³	3500	5 (at 77 K, 20 bar)	NA	NA

Table 3 The materials produced by thermally treating PEEK under different chemical environments have impressive H₂ gravimetric and volumetric uptakes compared to other pure and doped carbon materials presently being investigated. Materials in blue represent CO₂ derived products whereas those in red represent steam treated products. Materials being used for comparison are in black. § Note: All H₂ gravimetric uptake measurements done at 2 bar, 77K unless otherwise specified.

Additionally, high-pressure excess H₂ adsorption isotherms were achieved for PEEK-CO₂-9-80 (Figure 19). As has been stated previously, this material has an extremely large surface area (3,103 m²/g), which is particularly beneficial for achieving large excess H₂ gravimetric uptake values. Furthermore, this material has a large cumulative pore volume (>1 cm³) and small pore diameters (predominantly ≤3 nm). Both of these characteristics are ideal for creating a material optimized for H₂ storage. As such this material demonstrates an exceptionally large gravimetric uptake, ranging to ~5 wt.% at 77K and 20 bar (Figure 19). Furthermore, this corresponds to a H₂ volumetric uptake of ~35 g/L using the unaltered porous carbon density of ~0.7 g/ml. However, it should be noted that upon compression of 15 metric tons the density of this material was effectively raised to ~1 g/ml; this density corresponds to a H₂ volumetric uptake of ~50 g/L.

Initial experiments demonstrated that the compression do not have significant effect on the gravimetric capacity. Further work needs to be done to fully characterize these products, but it is obvious that these materials possess outstanding H₂ volumetric adsorption capacities. Furthermore, their large excess gravimetric uptakes (~5 wt.%) classify them as one of the best of any materials presently under investigation by the DOE.

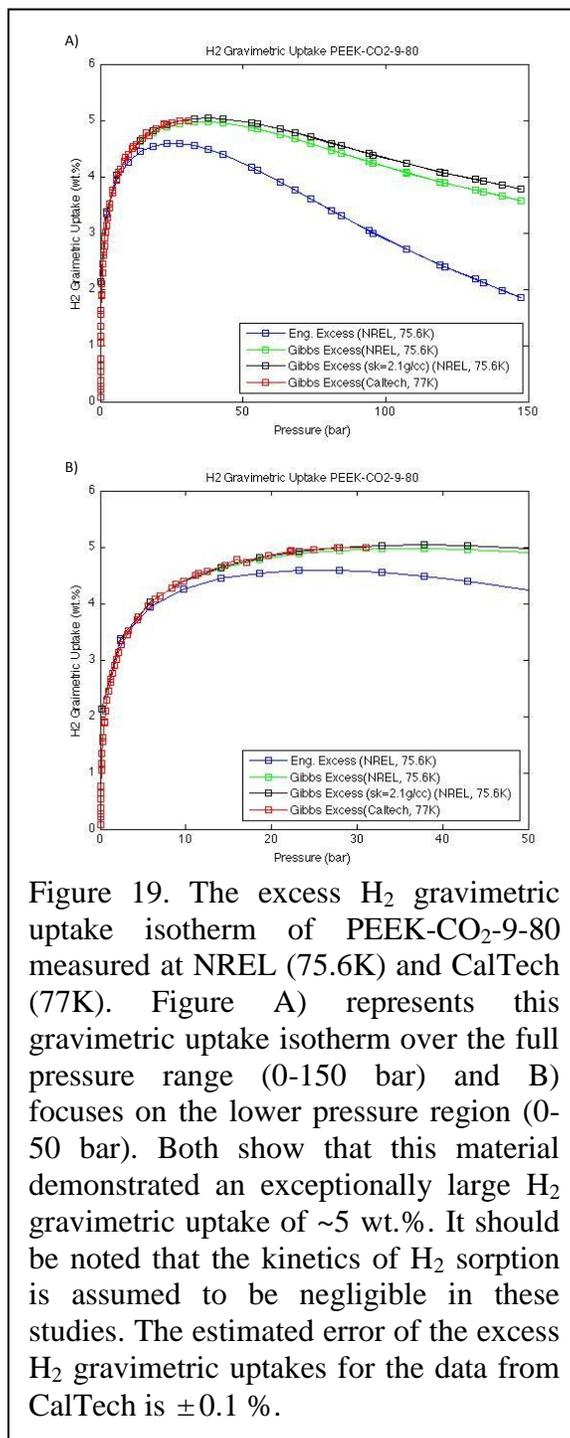


Figure 19. The excess H₂ gravimetric uptake isotherm of PEEK-CO₂-9-80 measured at NREL (75.6K) and CalTech (77K). Figure A) represents this gravimetric uptake isotherm over the full pressure range (0-150 bar) and B) focuses on the lower pressure region (0-50 bar). Both show that this material demonstrated an exceptionally large H₂ gravimetric uptake of ~5 wt.%. It should be noted that the kinetics of H₂ sorption is assumed to be negligible in these studies. The estimated error of the excess H₂ gravimetric uptakes for the data from CalTech is ±0.1 %.

It is evident that many factors are very important to the H₂ storage capabilities of these materials. Having a large surface area was known to be advantageous for achieving large H₂ uptake values. However, utilizing the parallel methods discussed in this paper, the importance of having large pore volumes and small pore diameters was shown. As such, it appears that a balance between surface area, pore volume and pore diameter must be optimized to achieve ideal H₂ storage conditions in porous carbon materials. Both steam and CO₂ treatments were used herein to controllably produce several materials with impressive excess H₂ uptakes, up to ~5 wt% and 35 g/L. These impressive H₂ sorption capacities are thought to be directly related to the balance between large surface area (~2000-3000 m²/g), large pore volume (>1 cm³/g) and small pore diameter (predominantly ≤3 nm) achieved in these materials.^{14,15}

3. Characterization of PEEK-CO2-9-80 at Southwest Research Institute to confirm the high hydrogen uptake:

10 grams of PEEK-CO2-9-80 were prepared at Duke and sent to different members within the Center and to Southwest Research Institute (SwRI) for independent hydrogen storage testing. The testing results from NREL and CalTech were discussed above. Official reports were also obtained from the SwRI. The measurements showed that the PEEK-CO2-9-80 demonstrated higher uptake among all carbon materials, even higher than AX-21. Figure 20 is from the test and shows the gravimetric uptake and volumetric capacity.

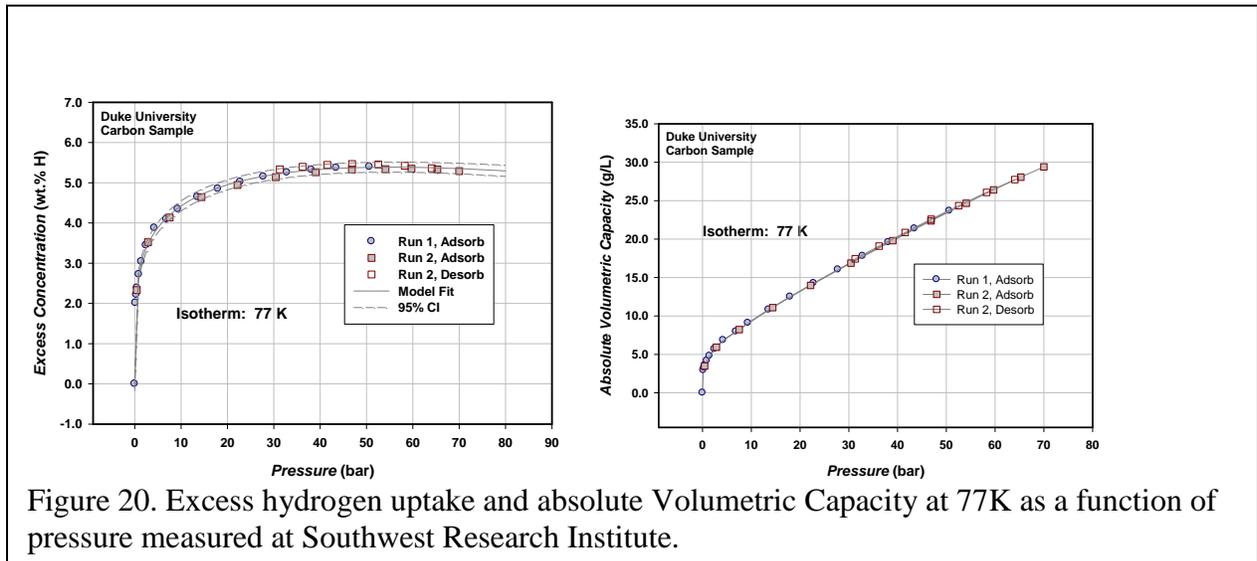


Figure 20. Excess hydrogen uptake and absolute Volumetric Capacity at 77K as a function of pressure measured at Southwest Research Institute.

It is worthwhile to note that there are assumptions made when obtaining the volumetric capacity. Through communication with Dr. Michael A. Miller at SwRI, we have obtained details of the assumptions and measurements:

- SwRI estimated the volumetric capacity semi-empirically by first measuring the intrinsic pore volume of the material from the room temperature hydrogen isotherm using the gravimetric technique, then apply the simplified local density (SLD) model to estimate the true skeletal density of the material and the adsorbed volume (essentially, the pore volume).

- The volumetric capacity is then estimated as the sum of the Gibbs excess adsorption (experimentally measured) plus the product of the estimated pore volume (SLD model) and the real-gas density at each pressure point in the isotherm curve.
- All real-gas densities were calculated from the Bender Equation of State.
- The skeletal density was estimated at 3.02 g/cc for the He-derived density. This high of a skeletal density is not unusual for a highly porous material.

To conclude: PEEK derived MPC materials is currently the best carbon based material for low temperature (77K) and high pressure (>20bar) hydrogen uptake. Measurements from 4 different labs: NREL, NIST, UNC and SwRI all confirmed the high uptake of hydrogen. The gravimetric uptake is >5%. However, the volumetric measurements still need to be further characterized, since SwRI showed ~30g/L at 77K and 70bar while estimates from simply measuring the bulk density of the materials gave ~35g/L capacity.

Patents: None

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